CEMENTITIOUS MATERIALS CHARACTERISATION BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY

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Abstract

Cementitious materials are widely used in radioactive waste disposal facilities and extensive national and international research programmes are implemented to understand the factors and processes affecting the release of safety relevant radionuclides from the disposal area. Characterising the cementitious materials in various states of degradation and correlate their sorption properties with their chemical composition is a main component of these research programmes. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is a characterisation tools that can be used to measure both major and minor elements in different cementitious materials. However, to effectively use it, the effect that major elements can have on the accuracy of minor elements measurement, as well as other interferences occurring in complex chemical systems such as cementitious materials, have to be identified and corrected. For CEM I and CEM II cements, an optimized mineralization procedure was developed, that is able to dissolve elements of interest like: Ca and Si as major elements, and Al, Fe, Mg, K and Na as minor elements. The resulted solutions were measured by ICP-OES applying two methods for matrix compensation: matrix matching and standard addition. The optimized method developed for measuring the major and minor elements by ICP-OES was tested on cement powders with known chemical composition in order to assess the recovery yields that can be further used to correct the measurement values for different cementitious materials.

Keywords: *Cementitious materials, Emission spectroscopy, Matrix effect*

Introduction

Due to their good retention properties for the most of the radionuclides, cementitious materials are widely used as component of the engineered barrier system of a disposal facility. In the surface repositories cement-based materials are used as conditioning matrix and also as structural materials, as these repositories generally consist of monolithic concrete structures located at or near the ground surface. In the geological repositories, cement-based materials are used mainly as component of the infrastructure (walls of the galleries and access tunnels), but also as material for the disposal container for long-lived radioactive waste.

The cement is a complex material composed of several anhydrous minerals, mainly calcium silicates formed from the reaction of calcium carbonate with silicate minerals (clays). Cement-based materials used in radioactive waste management consist of hydrated cement pastes (HCP), mortars and concrete. Hydrated cement pastes (HCP) contain a wide variety of sorption sites for the dissolved elements in pore water (either radioactive or chemical contaminants). Various sorption processes, from surface adsorption reactions to incorporation and solid-solution formation, occur on these sorption sites and depend on the radionuclide and porewater chemistry.

The experimental sorption studies are carried out to obtain specific data needed to model the radionuclides mobility through the disposal area (near-field), but also to understand the sorption processes. The experimental results have to be correlated with the studied materials composition, mainly with the hydration phases of the cementitious materials, but also with the content of the major (Ca, Si) and minor elements (Na, K, Mg, Fe).

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is one of the analytical methods used to measure most of the chemical elements in a multitude of samples, in principle in any type of sample that can be converted into liquid form, or from which the element of interest can be extracted in a liquid phase. This technique is based on the spontaneous emission of photons from atoms and ions, which were previously excited by absorbing energy from the plasma [1]. Liquid and gaseous samples can be injected directly into the instrument, while solid samples require extraction or mineralization to bring the elements of interest into liquid form. In order to measure the elements of interest from solid samples or slurries, it is necessary to process them to obtain clear solutions in which the elements of interest can be found.

Different mineralization methods, such as hot acid digestion (mineralization in a microwave field or in open vessel on an electric hot plate) or alkaline fusion, were developed for a wide range of matrices [2].

After being introduced as a solution in the emission spectrometer, the sample is transformed in the spray chamber into aerosols that are then directed to the central plasma channel, where they quickly evaporate at a temperature of about 10,000 °K. The elements to be analysed are released in the form of free atoms, in a gaseous state, and plasma provides sufficient energy to convert atoms into ions and bring them into excited states. Excited atomic and ionic species can relax to the ground state by emitting a photon with characteristic energy, determined by the structure of the atom or ion that emitted the photon. Consequently, the wavelengths of the photons can be used to identify the elements that emitted them.

The fundamental concept of atomic spectroscopy is the uniqueness of each element's energy level. Since each energy transition of an electron within an atom gives rise to a single photon, the number of atoms undergoing that transition determines the number of photons emitted and, consequently, the total number of photons of a certain wavelength is directly proportional to the concentration of the element in the analysed sample [1].

ICP-OES is characterized by a very rich spectrum; the 70 elements that are usually determined by ICP-OES give rise to at least 70,000 emission lines in the wavelength range between 200 nm and 600 nm. Even with such a rich spectrum, ICP-OES is considered a technique with less interference compared with other commonly used atomic spectroscopy analytical techniques.

The plasma formed by argon is inert compared to the chemical reactivity of a flame used in other spectrometric systems (such as atomic absorption spectrometers). Also, the high temperature of the plasma helps reducing the chemical interferences. The temperature is high enough to decompose most species into atoms or ions that will then be excited to record the wavelength emitted by returning to the ground state.

However, interferences also appear in ICP-OES and can be caused by several effects, such as matrix, sample transport, ionization, intensification or diminution of the emission response, or spectral overlaps. These interferences occur especially in applications that measure different elements in complex samples containing elements with both high and low concentrations.

Two large categories of interferences can be observed in ICP-OES: non-spectral interferences (including physical and chemical interferences) and spectral interferences. If non-spectral interferences are detected and not corrected for, false positive responses will arise and be reported as the concentration of the element of interest. Since the inductively coupled plasma has enough energy to excite almost any element that is introduced into the plasma, the obtained spectra are most often very "rich" for complex and concentrated samples. Spectral interferences represent the effect of background emissions due to recombination phenomena, stray light from the emission of an element in high concentration, the overlap of a spectral line of another element or overlaps of molecular spectra [3].

As cementitious materials are quite complex systems in which the element of interest can be found in high concentration levels (such as Ca and Si), but also in low concentrations (such as K, Na, Mg, Fe), applying the ICP-OES technique to measure the concentration of major and minor elements requires special care in identifying and solving the interferences that can occur and affect the accuracy of the measurements.

Materials and methods

Sample preparation for ICP-OES analysis

To be able to measure the concentration of different elements in a cementitious sample by using ICP-OES, the elements of interest must be extracted into a liquid phase. For this study, microwave digestion was applied to prepare the cementitious samples for analysis by emission spectroscopy. Four different cement powders made up the cements for which mineralization tests were conducted: one ordinary Portland cement (CEM I, produced by LAFARGE Val d'Azergues factory) containing 97% clinker and 3% minor auxiliary components, and the following three composite cement powders:

- CEM II A - S 42.5R (produced by Heldemberg factory), containing clinker between 80 and 94%, blast furnace slag between 6 and 20% and other minor auxiliary components between 0-5%;
- CEM II/B-M (S-V-LL) 42.5R (produced by Holcim), containing clinker between 65 and 75%, blast furnace slag, fly ash and limestone between 21 and 35%, and other minor auxiliary components between 0-5%;
- CEM V/A (S-V) 42.5N (produced by Calcia Romba factory), containing 52% clinker, 23% blast furnace slag, 24% fly ash, and 1% secondary constituents.

For CEM I and CEM V powders, the powders product sheets containing the corresponding oxides compositions were available from the manufacturers, these data being used to calculate the recovery yield for the oxides of interest. For various cementitious samples that are subjected to a similar matrix dissolution procedure, the computed recovery yields can be utilized to adjust the oxide content.

The cement-based samples were mineralized using an Anton Paar Multiwave 3000 digestion system and a digestion reagent consisting of a mixture of nitric acid (HNO3), hydrochloric acid (HCl), and hydrofluoric acid (HF).

For the cement pastes mineralization, two digestion steps at 200 °C (15 minutes each) and another two digestion steps at 240 °C (30 minutes each) were applied, representing a combination and adaptation of three digestion methods recommended by the manufacturer for cement, slag and ash, respectively. In all digestion steps, the temperature in the digestion tubes was increased in 2 intermediate steps: 160 °C and 180 °C.

Since the liquids produced are analysed by ICP-OES, it is necessary to remove HF from the samples in order to avoid damaging of the sample introduction system components (nebulisation chamber, nebulizer, and torch). The HF was eliminated by complexation with boric acid (H_3BO_3).

Wavelengths selection and verification of the matrix effect

For determining the elements of interest in cementitious materials, iCAP 6500 spectrometer produced by ThermoScientific, with dual plasma viewing (axial and radial) was used.

The elements of interest to be analysed by ICP-OES are Ca, Si, Al, K, Na, Fe and Mg. The problems regarding matrix effects could be caused by the presence of Ca in high concentrations (45%, generally), but also of Si (~10%). The emission lines selected for the analysis of each element of interest must have good sensitivity and be free of spectral interferences. If the interference cannot be avoided, corrective measures have to be applied. Analyzing the emission lines of the elements of interest, it was found that, for example, the emission lines of Al at 309.284 nm and 396.152 nm are not suitable for Al analysis due to a partial overlap with emission line of Ca. There were situations, for example for Na, K, Ca and Mg, in which two emission lines were initially chosen, but after performing spectrometer calibration and determining the recovery yield of the elements to be analyzed from a verification solution and checking the emission peaks, other emission lines were selected for further analyses. Table 1 presents which emission lines were selected for ICP-OEP analysis, for the elements of interest.

Table 1. Emission lines selected for ICP-OES analysis of cement based materials

Element	Wavelength of the emission line, [nm]
Ca	317.933
Si	251.611
Al	308.215
Na	589.592
K	766.490
Fe	259.94
Mg	285.213

The magnitude of the matrix effects given by Ca and Si (as major elements in cement), but also by Al (even this element has a lower concentration than Ca, it can be easily ionized giving interferences for other elements of interest), was evaluated by measuring the intensities given by the analytes in solutions with constant concentration (5 mg/l) and different concentrations of the matrix (Ca, Si, Al). The matrix effect was calculated using the equation below:

$$M\% = \frac{(Im - In)}{In} \times 100 \quad (1)$$

where: *Im* represents the net emission intensity of the element of interest in the presence of the matrix, and *In* represents the net emission intensity of the element of interest in 2% nitric acid solution.

Calibration of emission spectrometer

The matrix to be analyzed by emission spectrometry with inductively coupled plasma influences the efficiency of the nebulisation process.

Although a simple concept, the nebulisation process can be a mechanism by which an acid can affect the emission line of the elements to be analyzed. An increase in the concentration of dissolved salts can lead to the solution viscosity raise, which in turn decreases the uptake rate of the solution to be analyzed. This implicitly leads to a decrease in the amount of analyte transported in plasma and causes a reduction in the analyte emission intensity.

In general, the ICP-OES measurements are performed with a nebulisation efficiency of 1%, which means that 1% of the sample volume introduced into the nebulisation system reaches the plasma, while the remaining 99% is eliminated through the exhaust system of the spraying chamber. The nebulised solution consists of very fine particles, similar to a fog, with diameters less than 8 μm.

If a matrix component changes the nebulisation efficiency from 1% to 0.8%, then the intensity emitted by the analysed element is decreased by 20%. A change in acid concentration of the analysed sample from 5 to 10% can cause a decrease in nebulisation efficiency between 10 and 35%, depending on the acid used, nebulizer type, the gas flow rate, and the coolant. To obtain results with good accuracy, it is necessary to match the matrix of the standards used for spectrometer calibration with that of the samples to be analysed, within a relative error of 1%.

The standards for spectrometer calibration were prepared by appropriately diluting a volume of monoelement ICP standard with a concentration of 1000 mg/l in 100 ml volumetric flasks with the same acid composition as the samples to be analysed.

As cement based materials are complex systems, adequate measures to resolve the matrix effect have to be implemented to ensure the results accuracy. The measures are decided based on the results of testing the effect of major elements on the minor elements measurement, tests that are described below.

Results and discussion

Experimental verification of the matrix effect

Tests performed to verify the effect of the major elements on the response given by the minor elements indicated that the presence of Ca significantly changes the emissions of all other elements of interest, these changes manifesting both in the emission signal decreasing and intensification. The emission intensities for Al, Na and K significantly increase as the Ca concentration in solution raise up to 300 mg/l, while the intensity of Si, Fe and Mg decrease with increasing the Ca concentration in solution.

Among the analysed elements, Mg is less affected by the presence of Ca, but the emission intensity of this element also decreases by 1% for Ca concentrations up to 300 mg/l, and by 3% for higher Ca concentrations. The emission signal of Al is the most affected by the presence of Ca in solution, a Ca concentration as low as 100 mg/l producing an enhancement of the emission response of Al by ~11%, while a Ca concentration of 800 mg/l enhances Al emission response by ~14% (calculated using Eq(1)). Similar, the matrix effect for Si was between 3% and 15%, for a Ca concentration of 100 mg/l and 800 mg/l, respectively.

In the test to verify the Si presence effect on the signal given by other elements, it was also noticed that high Si concentrations modify the emission signals of other elements. The signals given by Mg, Na, K and Al are amplified, while the emission signals of Ca and Fe are suppressed (decreased). The effect of Si on Al emission is relatively small compared to that of the other elements. The presence of 200 mg/l of Si produces an increase in the Al signal of ~2%, but the emission intensities of Mg, K, Na and Fe are severely affected by the presence of Si in the analysed solution.

In general, it was observed that the emission intensities of the elements are modified by the presence of the major elements in the matrix. The matrix effect given by the presence of Ca and Si in high concentrations compared to the concentration of other elements is probably a complicated function of many parameters, such as the operating conditions of the spectrometer, the number of particles in the plasma, the ionization potential of different elements, the total excitation potential of the analytical lines etc. [4].

Blades and Horlicks explained the enhancement or suppression of the emission intensity of the element to be analyzed in the presence of matrix elements based on the change in the balance between atom (A), ion (A^+) and electron (e^-) [5]:

$$A \Leftrightarrow A^+ + e^- \quad (2)$$

In certain situations, the addition of the major element in the matrix leads to an increase in the density of electrons in the plasma, which causes the balance to be shifted towards neutral atomic species with the effect of intensifying the atomic emission. If the shift in ionization equilibrium accounts for the emission intensity raise, the degree to which the emission intensity changes depends on the number of electrons in the plasma that is changed by the introduction of the major matrix element(s).

Other researchers [6] suggested that the intensification of the emission intensity may be caused by the increase in the collision rate due to the increase in the electron density. The higher the kinetic energy of the electron is, the greater the probability of ion–electron collision, which leads to excitation rather than recombination. The degree of ionization will be also reduced by charge transfer reactions between the matrix atom (M) and the ion to be analyzed (A+):

$$A^+ + M \Leftrightarrow M^+ + A \quad (3)$$

Spectrometer calibration and analysis of solutions obtained by cementitious samples digestion

As the tests performed to verify the matrix effects indicated suppression of the emission signal given by the minor elements in the presence of the major elements (Ca and Al), it was decided to apply two methods to overcome the matrix effect, namely: *matrix match (MM) method* and *standard addition (SA) method*.

For the MM method, the spectrometer is calibrated using standards that contain similar amounts of major elements as in the samples to be analyzed, and also the same amounts and types of acids.

In addition, 5 ppm of Ytriu were added both in the samples to be analysed, and in the calibration standards, Yttrium being used as an internal standard to correct physical and chemical interferences that could affect the results accuracy.

For the SA method, samples without addition and samples with addition of elements of interest are measured, and the concentration of the elements in the sample is calculated by interpolation, using a linear regression.

As both Ca and Si present in the samples to be analysed affect the minor elements emission, it was decided to apply for sample mineralization two sequential steps, aiming to solubilise in the first step all oxides excepting silicon oxide, and in the second stage the silicon oxide, according to diagram presented in Fig. 1. The ICP-OEP measurements were performed separately on the solutions resulted from the 1st and 2nd mineralization steps.

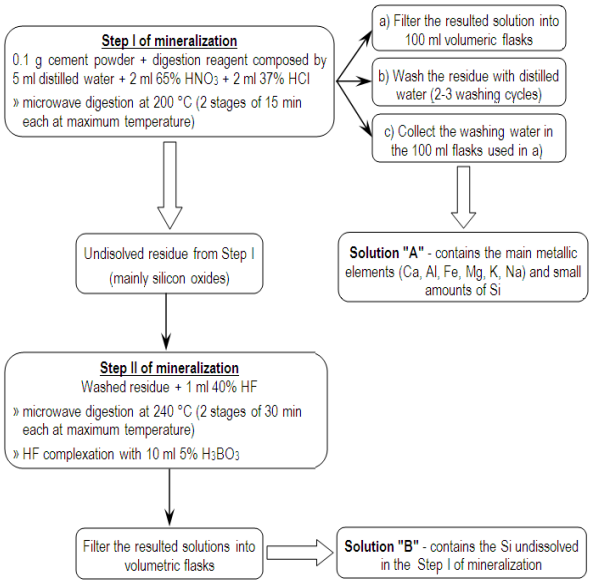


Fig. 1. Optimized mineralization procedure for cementitious materials

Matrix match (MM) method

In the solutions obtained from the 1st mineralization step, silicon oxide should be absent, or if it was extracted it should be in sufficiently low concentrations to not influence the emission lines of other element of interest. Instead, most of the Ca content of the cement powders should be solubilised in this solution.

To add the correct amount of Ca in the calibration standard, the Full Frame option of the iCAP 6500 spectrometer was used. Applying this option, all elements in the solutions to be analysed can be identified, and a semi-quantitative analysis of their concentration is performed based on the analysis of a blank and of a simple calibration solution containing the identified elements. The Full Frame analysis of the samples obtained from the 1st mineralization step indicated presence of Ca with about 400 mg/l concentration and of Si with a concentration around 10 mg/l, almost 10 times less than the Si concentration for which matrix effect was observed.

Based on the results obtained using the Full Frame option, it was decided to measure the concentrations of Al, Fe, Mg, K and Na directly in the solutions obtained from the 1st mineralization step. In each solution, 5 mg/l of Y (used as internal standard) was added.

Five combined calibration standards were prepared in the concentration range of (0 – 40) mg/l for Al, Fe and Si, (0 – 20) mg/l for Mg, (0 – 10) mg/l for K, and (0 – 4) mg/l for Na, respectively. The calibration standards for Al, Fe, Mg, K and Na analysis contain, in addition to the adequate concentrations of these elements, appropriate amount of nitric acid and hydrochloric acid (2 ml HNO_3 and 2 ml HCl in the 100 ml volumetric flask), 400 mg/l of Ca (to match the matrix of the samples to be analysed), and 5 mg/l of Y (as internal standard, also added in the same concentration to the analysed solutions).

Since Ca is characterised by emission lines with high intensities being present in high concentration in the solutions obtained by cement powders mineralization, these solutions were diluted by a factor of 100, before Ca analysis by ICP-OES. Five Ca calibration standards in the concentration range of (0 – 6) mg/l were prepared, each containing 2 ml HNO_3, 2 ml HCl, 5 mg/l of Y and distilled water to 100 ml.

ICP-OES analyses were performed with 30 sec. integration time and 120 sec. washing time, to avoid contamination between the analysed samples. The calibration curves using the above-described standards were linear, with very good correlation coefficients for all elements (>0.999). The quantification limits (MDL) for the analysed elements, determined as average of 15 non-zero values measured on the calibration blank, indicated that all elements can be measured with good accuracy for concentrations as low as few μg/l.

To analyse the solutions obtained after the 2nd mineralization step, containing mainly Si, five Si standards in the concentration range (0 – 200) mg/l were used to calibrate the spectrometer. The calibration standards were prepared in 100 ml volumetric flasks, and to match as much as possible the matrix of the solutions to be analysed, for each standard 1 ml of HF and 10 ml of H_3BO_4 were added, as well as 5 mg/l of Y and distilled water to 100 ml volume. The calibration curves of the spectrometer were linear for both emission lines selected for Si measurement (correlation factors > 0.999), and the Si concentration values measured at the 2 wavelengths (212.412 nm and 251.611 nm) differed by less than 2%, confirming the good accuracy of the results.

After measuring the elements of interest concentration, the concentrations of the corresponding oxides were calculated (values reported in Table 2) using adequate element to stoichiometric oxide conversion factors [7].

Table 2. Oxides composition of the analysed cement powders, [mg/g]

	CEM I	**CEM II A-S**	**CEM II/B-M**	**CEM V**
CaO	623.42	609.51	576.73	46.25
Al_2O_3	34.50	50.01	49.19	102.84
Fe_2O_3	48.67	27.55	22.16	30.21
MgO	4.83	20.78	19.02	26.49
K_2O	6.53	8.09	8.31	14.18
Na_2O	1.38	0.23	0.19	2.28
SiO_2 from 1st mineralization step	16.70	17.29	10.37	12.95
SiO_2 from 2nd mineralization step	190.96	197.44	186.72	243.94

The oxide compositions for CEM I and CEM V were used to calculate the recovery yields for each oxide (presented in Table 3). As it can be seen in Table 3, excepting for Ca in the CEM V sample, which was recovered with an extremely low yield, all metallic elements that were analysed were recovered with high yields in both cement powders. The total recovery yield for SiO_2 was also very good, with most of the SiO_2 dissolved in the 2nd mineralization step, in which fluoric acid was used.

Table 3. The recovery yields

	CEM I	**CEM V**
CaO	95.18	9.78
Al_2O_3	101.48	100.83
Fe_2O_3	97.33	91.56
MgO	98.55	98.09
K_2O	97.53	99.83
Na_2O	98.63	99.23
SiO_2 from 1st mineralization step	7.99	4.40
SiO_2 from 2nd mineralization step	91.37	82.97

In case of CEM V cement powder for which the complete dissolution of the matrix was not achieved, the recovery yield of silicon oxide is lower than for the ordinary Portland cement (CEM I), which mostly contains clinker. Ca was also very low recovered from CEM V composite cement powder.

Further tests have to be performed to optimize CEM V cement dissolution, in any combination of acids and maximum temperature at which the digestion system operates this cement was not completely dissolved. As alternative to the microwave digestion, alkaline fusion with lithium tetraborate and/or sodium carbonate will be tested for cementitious materials based on CEM V.

Standard addition (SA) method

The standard addition method cannot be applied for Ca measurement in the solutions obtained from 1st mineralization step as Ca concentrations are around 400 mg/l. Application of SA method requires Ca standard with a much higher concentration than the available ICP standards (usually in concentration up to 1000 mg/l).

To determine the content of Al, Fe, K, Mg, Na and Si in the solutions obtained from 1st mineralization step, a blank sample was prepared, containing nitric acid and hydrochloric acid, and 3 sub-samples from each of the solutions to be analysed, one without standard addition (Spike 0) and 2 sub-samples containing standard additions in different concentrations (Spike 1 and Spike 2).

Sample measurements using the SA method consists in spectrometer calibration using a blank sample and the three sub-samples (Spike 0 ÷ 3). The essential condition in this method is to obtain linear regression curves between the elements emission intensities in analysed sub-samples and the concentration added in samples with standard addition. The elements concentration in samples without standard addition is calculated by extrapolation. Linear regression curves were obtained for all elements, with very good correlation factors (>0.999; see Fig. 2 for Al and Fe).

The results obtained for the concentration of the elements of interest in the solutions from the 1st mineralization step are presented in Table 4; the results obtained for the same elements by the matrix matching method are included for comparison. In general, the element concentration values measured by SA method are slightly higher than those obtained by MM method, but the differences are less than 20%, being within the cumulative error associated with measurements by emission spectrometry of the elements in solid samples (considering both sample preparation and measurement). The SA method has the advantage that is faster and does not require preliminary analyses to identify matrix effects and taking countermeasures. However, to add the appropriate amount of standard, which usually has to be at least twice the concentration of the elements to be measured, the order of magnitude of the concentration of the elements of interest must be known. The emission spectrometer's Full Frame option can be used to do this.

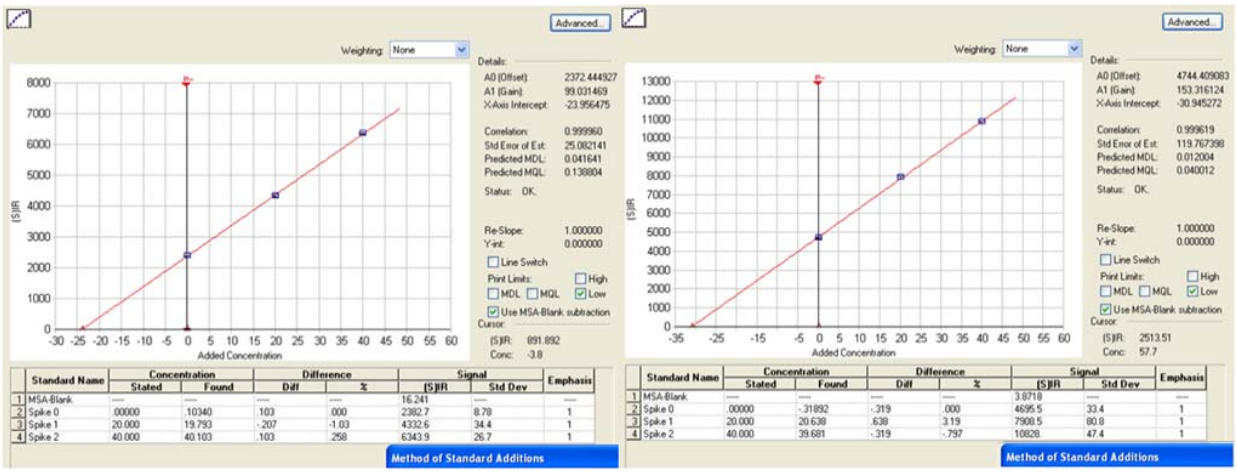


Fig. 2. The regression curves used to calculate Al concentration (left) and Fe concentration (right) in the solutions without standard addition

Table 4. Concentration of the element of interest [mg/l] measured by SA and MM methods

	Al		Fe		K		Mg		Na		Si	
	SA	MM	SA	MM	SA	MM	SA	MM	SA	MM	SA	MM
CEM I	23.93	22.04	23.07	22.05	7.80	7.28	8.10	6.47	0.12	0.14	9.46	8.03
CEM II A-S	30.54	27.21	24.79	19.81	7.24	6.90	14.92	12.89	0.18	0.18	9.87	8.31
CEM II/B-M	30.72	26.90	19.90	16.01	7.67	7.13	13.75	11.85	0.16	0.14	6.13	5.01
CEM V	89.04	79.65	64.93	57.11	28.62	22.76	20.37	17.49	0.14	0.13	7.51	6.16

Conclusions

Two challenges were encountered in developing an adequate method for major (Ca and Si) and minor (Al, Fe, Mg, K and Na) elements measurement in cementitious materials by ICP-OES: 1) finding the adequate method for matrix dissolution, and 2) selecting the optimal conditions for measuring the emissions given by the elements of interest in a complex matrix such as the one obtained by mineralization of cementitious materials.

For the cement-based materials mineralization, a sequential digestion procedure was successfully optimized for CEM I and CEM II cements.

In the 1st mineralization step, the metallic elements (Ca, Al, Fe, Mg, K and Na) were dissolved in the presence of concentrated nitric and hydrochloric acids at 200 °C. In the 2nd step, the undissolved residue from the 1st step, consisting mainly in silicon oxides, was dissolved with concentrated hydrofluoric acid at 240 °C. By applying this procedure for CEM V, a white precipitate was observed, which contains Ca most probably, while the silicon oxides were not completely dissolved. Alkaline fusion with lithium tetraborate and/or sodium carbonate will be further tested for cementitious materials based on CEM V.

The tests performed to verify the matrix effect indicated that the major elements (Ca and Si) significantly change the emission intensities of the minor elements (Al, Fe, K, Mg, Na). To correct the matrix effects, two methods were tested: 1) matrix match (MM) method - calibration of the spectrometer with standard solutions in matrices close to the matrices of the solutions to be analysed, complemented with the use of an internal standard (Yttrium), and 2) standard addition (SA) method. Similar results were obtained by the two methods, with relative deviations less than 20%. The SA method has the advantage of a shorter time to prepare the solutions for ICP-OES analysis and does not require preliminary analyses to identify matrix effects and implement countermeasures.

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