

## Concrete de-formulation: contribution of electron microscopy techniques and image analysis

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### INTRODUCTION

In an industrial context, it is common to be faced with external requests (such as litigation) leading to a desire to know the composition of a concrete from a building site to a more or less advanced degree. Concrete de-formulation topics are born from the desire to better understand and master concrete de-formulation strategies, in order to be more prepared, efficient and reactive when litigation cases are handled. The de-formulation of concretes is indeed a rather complex field, because of the diversity of cases encountered, despite the existence of standards and reference documents on this subject [1-6]. It can indeed be applied to various types of concretes with very variable compositions, for example in the case of problems of resistance, cracking or setting up, durability issues, etc. It could be also useful in the case of the protection of the industrial property (with respect to patents for special concretes).

In the case of litigation, the main information sought is usually the initial water and cement contents of the formula. The analytical approaches described in the standards and some studies [1-6] make it possible to obtain an estimate of these values, with accuracy being even lower when the concrete formula is complex, and in particular in the case of concretes containing SCMs. We have studied these different methods, their advantages and their experimental limits on concretes with relatively simple formulation. Then we have compared and described these methods in terms of evaluation of source of error, associated assumptions, uncertainty and robustness. It appears that further work is needed towards the identification, development and evaluation of alternative methods that are more adapted to cases for which the conventional methods do not give satisfactory results. In this context, approaches of selective fragmentation of concrete, mass balance calculation and SEM observations were tested to propose an approach to concrete de-formulation that can be potentially applicable to a field of formulation much broader than what the classical methods covered with relevance.

## SEM OBSERVATIONS

Qualitative scanning electron microscope (SEM) observations on concrete samples were first used to describe qualitatively the concrete sample, with determination of the presence of supplementary cementitious material (SCM) or residual cement particles, aggregates characterization (sizes, chemistry), porosity, etc. SEM observations can identify siliceous or calcareous filler, fly ashes, slags, silica fume, pozzolans, aggregates, hydrates and anhydrous cement. However, metakaolin and some fine particles of silica fume are difficult to detect. The determination of such characteristics can help the selection of the best de-formulation approaches to use. A quantitative method using SEM observations was developed [7-8] and used in the scope of concrete de-formulation. The main difficulties to overcome when observing concrete by SEM are the representativeness of the studied sample and the observation of elements of sizes from microns to centimetres. To overcome this last difficulty, a combination of two different observations was developed, the first one being done on a large sample to observe macrostructure, and the second on a smaller sample to observe microstructure, as described in Table 1, along with illustrations of the SEM phase classification results from each scale (Figs. 1 and 2).

*Table 1: Main parameters of the two distinct SEM observations used for concrete de-formulation.*

	Large concrete sample	Small concrete sample
Observation objectives	Macrostructure: Qualitative and quantitative description of large elements (>80 $\mu\text{m}$ ) Paste/aggregates ratio	Microstructure Qualitative and quantitative description of small elements (<80 $\mu\text{m}$ )
Sample size	Concrete disc with diameter ~11 cm	Polished section with diameter ~4 cm
Sample preparation	Fast polishing (~1 hour)	Fine polishing after epoxy impregnation (1 to 2 weeks)
Size of observed zones	~40 cm	~5 mm <sup>2</sup>
Pixel size	9.9 $\mu\text{m}$	0.354 $\mu\text{m}$
Minimal size of visible objects	Around 80 $\mu\text{m}$	Around 1 $\mu\text{m}$
Results	Surface fractions of aggregate by nature, matrix, and macroporosity Estimation of chemical composition of aggregate skeleton Description of morphology of large elements, porosity distribution, ...	Surface fractions by nature of aggregates, SCM, hydrates, residual cement, microporosity Estimation of chemical composition of SCM Description of morphology of small elements

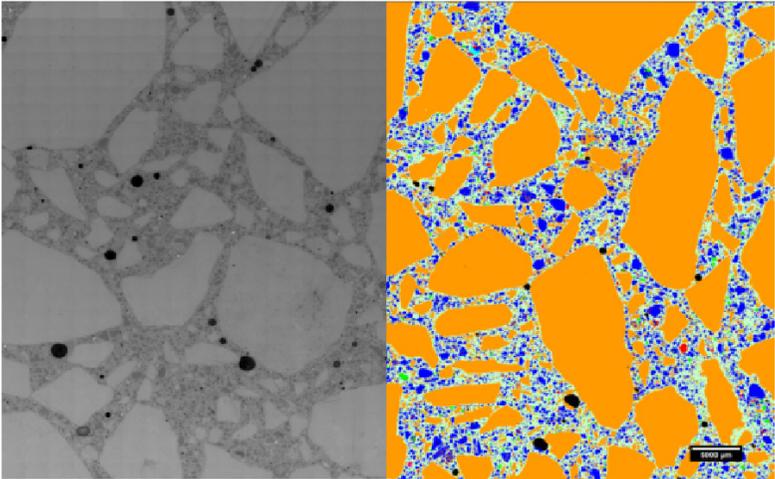
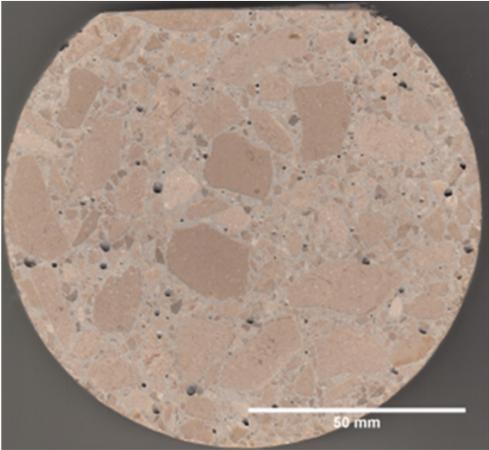


Figure 1: Large concrete sample (top) and corresponding SEM phase classification (bottom).

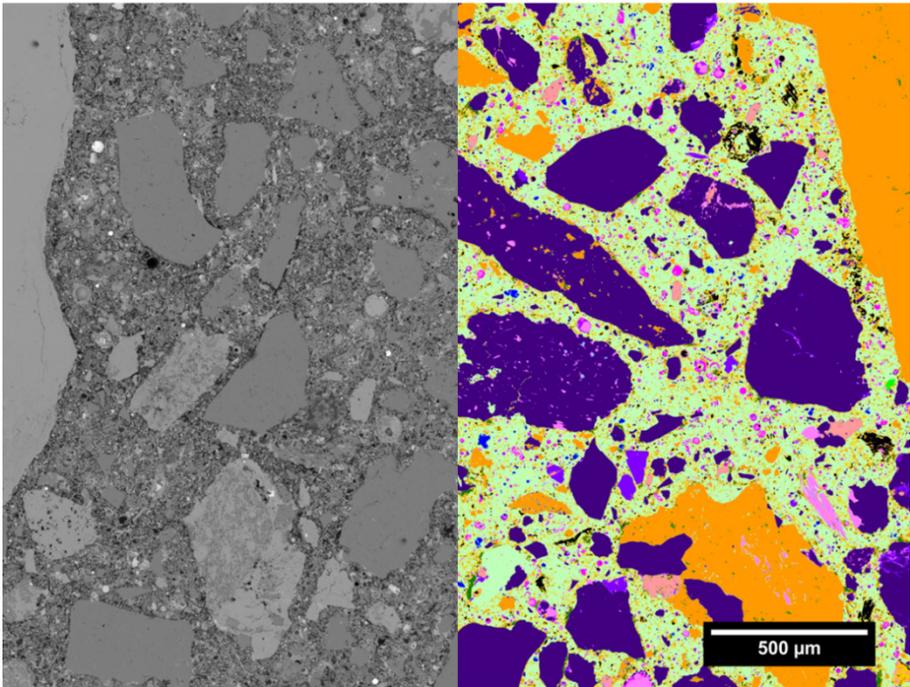
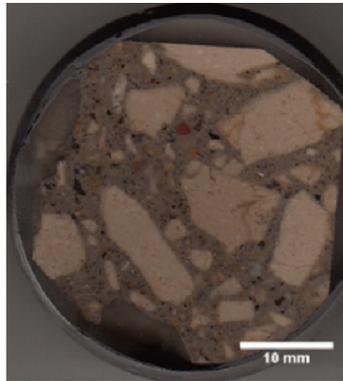


Figure 2: Small concrete sample (top) and corresponding SEM phase classification (bottom).

#### CALCULATION METHOD BASED ON SEM OBSERVATIONS

The data resulting of the image treatment of each observed surface are then combined to obtain a description of the whole concrete, with surface percentage of each component, as shown in Figure 3.

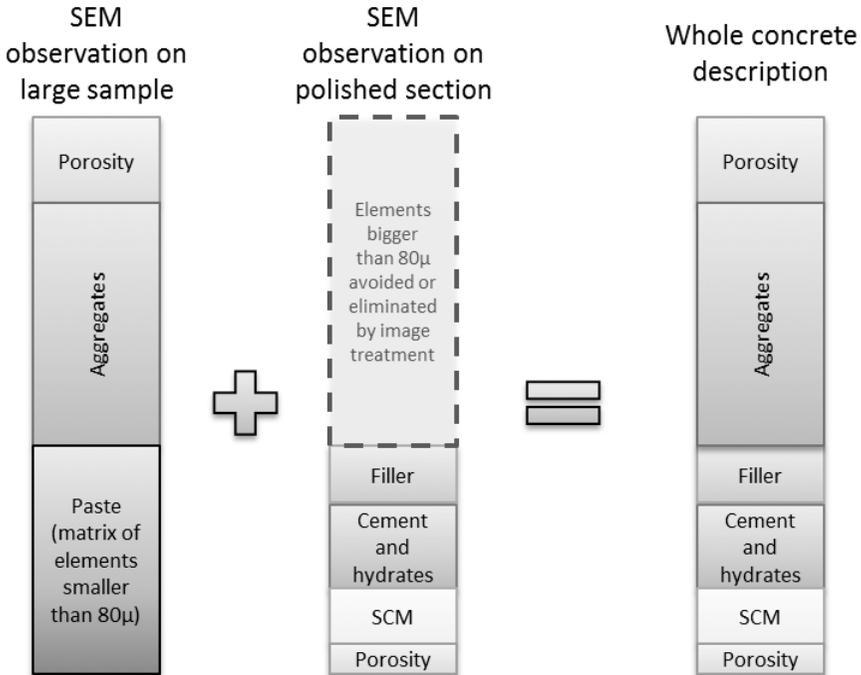


Figure 3: Estimation of each component surface percentage by combining two SEM observations

From SEM observations and image treatment results done on large sample (disc) and polished section (PS), the surface percentage of each component can be estimated in the whole hardened concrete using the following equation:

$$\%sX(\text{concrete}) = \%X(\text{disc}) + \%X(\text{PS}) * \frac{\%matrix(\text{disc})}{100}$$

With:

$\%sX(\text{concrete})$  = Surface percentage of component X in the whole hardened concrete

$\%X(\text{disc})$  = Surface percentage of component X measured on large sample

$\%X(\text{PS})$  = Surface percentage of component X measured on polished section

$\%matrix(\text{disc})$  = Surface percentage of matrix (paste) measured on large sample

Considering that surface percentages are equivalent to volume percentages, these values can be converted to mass percentages:

$$\%mX(\text{concrete}) = \frac{\%sX(\text{concrete}) * Dx * 100}{\sum[\%sXi(\text{concrete}) * Dxi]}$$

With:

$\%mX(\text{concrete})$  = Mass percentage of component X in the whole hardened concrete

$\%sX(\text{concrete})$  = Surface percentage of component X in the whole hardened concrete

$Dx$  = Density of component X in g/cm<sup>3</sup> (estimated values with for example 3 for cement, 2 for hydrates, 2.3 for fly ashes, 2.6 for aggregates)

$\Sigma[\%sXi(\text{concrete}) * Dx_i]$  = Sum, for all the elements measured, of the products of the surface percentage of an element Xi by the density of this same element

The measured hydrate fraction can be separated between anhydrous cement and bound water, using the loss on ignition value between 80°C and 550°C. This gives a percentage of total anhydrous cement estimated as the sum of the percentage of anhydrous cement observed by SEM and the percentage of hydrates decreased by the amount of water bound:

$$\%mCt(\text{concrete}) = \%mC(\text{concrete}) + \%mHyd(\text{concrete}) - \%Wbound$$

With:

$\%mCt(\text{concrete})$  = Total anhydrous cement percentage measured on hardened concrete

$\%mC(\text{concrete})$  and  $\%mHyd(\text{concrete})$  = mass percentages of anhydrous cement and hydrates respectively estimated by SEM observations

$\%Wbound$  = Mass percentage of bound water measured by loss on ignition between 80°C and 550°C

These mass percentages calculated on hardened concrete can be converted to mass percentage on initial concrete (initial content of each component) by using the free water content estimated by water porosity. The initial mass of each component per m<sup>3</sup> of concrete is obtained using fresh density calculated as the sum of hardened concrete density (water porosity measurement) and free water content.

$$\%mXini = \frac{\%mX(\text{concrete}) * (100 - \%Wfree)}{100}$$

$$mXini = \frac{\%mXini * Df}{100}$$

With:

$\%mXini$  = Initial content (percentage) of component X in concrete

$\%mX(\text{concrete})$  = Mass percentage of component X in the whole hardened concrete

$\%Wfree$  = Mass percentage of free water, measured by water porosity

$mXini$  = Initial mass of component X in kg/m<sup>3</sup> of concrete

$Df$  = Fresh density

Using this approach combining SEM observations, loss on ignition and water porosity, the whole concrete can be described, and the percentages of all components can be estimated separately.

## RESULTS ON FOUR MODEL CONCRETES

This approach was used on the same basis of model concretes with increasing complexity (Figure 4). The aim was to highlight strengths and weaknesses of each approach on various types of concrete formulations.

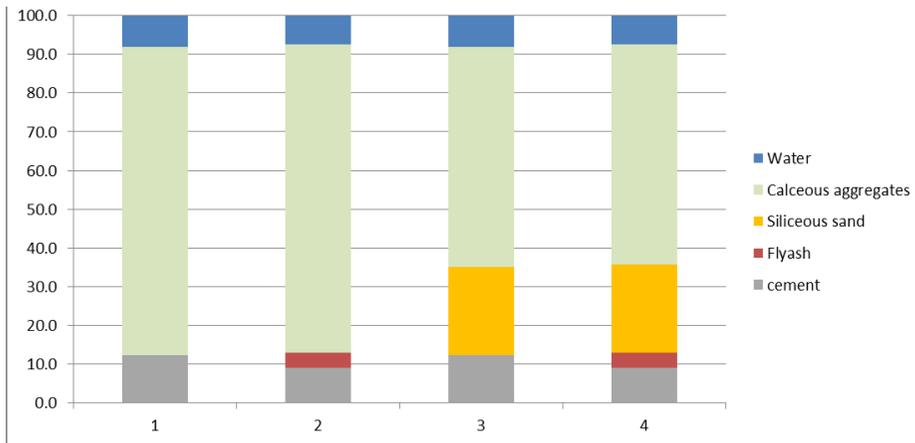


Figure 4: Formulation of four different model concrete samples

The main results are summarized in Table 2. The initial cement contents (in kg per m<sup>3</sup> of concrete) measured by SEM are compared to theoretical values for the four concretes studied.

Table 2: Estimated cement (or other components) contents, (kg/m<sup>3</sup> of concrete).

	Concrete 1		Concrete 2		Concrete 3		Concrete 4	
	Theory	Meas.	Theory	Meas.	Theory	Meas.	Theory	Meas.
Water content from LOI	189	189	174	178	189	190	174	176
Cement	290	287	213	227	290	360	213	240
Fly ash	-	-	91	43	-	-	91	36
Aggregates	1874	1812	1874	1861	1868	1782	1868	1905

## CONCLUSIONS

SEM observations are promising to estimate the initial content of all concrete components, even on a complex formulation. Except concrete 3 (probably due to a formulation issue during concrete preparation or sampling issues with inhomogeneity), the calculated cement contents are satisfactory for all the other samples. Fly ash contents are underestimated and the method could be improved by taking into account that these particles are porous. Finally, a concrete de-formulation approach by combining two SEM observations is really promising for unknown

concretes or concretes containing SCM. Even if a few sources of uncertainties can be described, this approach allows theoretically the estimation of initial formula and initial content of each component (except particles smaller than 1 $\mu$ m) without any knowledge of concrete formulation and chemistry of components. This method, however, requires a quite long time with sample preparation, data acquisition and image treatment.

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