

Analysis of cement paste and aggregate content of concrete using micro X-ray fluorescence

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Abstract

A new method for determining the cement paste, fine aggregate and coarse aggregate content of hardened concrete using micro X-ray fluorescence (μ XRF) is presented. The method involves mathematical and morphological operations to extract aggregate particles from large-area ($100 \times 50 \text{ mm}^2$) composite element maps acquired with μ XRF. The method was tested on five concretes containing different types of aggregates including gravel, limestone, siliceous sand, and sintered lightweight aggregates. The results were compared against point count analysis and data from the actual mix design. The average errors in relation to the mix design for the measured fine aggregate, coarse aggregate, total aggregate, cement paste contents and fine/coarse aggregate ratio were 12%, 12%, 3.4%, 10%, and 27% respectively. All measured values fell within $\pm 4\%$ of those point-counted. An image size of $> 2000 \text{ mm}^2$ (at least five times maximum aggregate size) was found to be required to obtain representative results. The advantages and limitations of the proposed method are discussed.

Keywords: Aggregates; Microstructure; Microscopy; Paste; Testing, apparatus & methods

1 Introduction

Concrete is a multiphase composite material made from cement, water, fine aggregate (e.g. sand) and coarse aggregate (e.g. gravel or limestone). The type and proportions of the constituent materials have significant effects on the engineering properties of concrete. For example, the cement content and water-to-cement (w/c) ratio determine the mechanical properties and long term durability of concrete (Neville, 2011, Mehta and Monteiro, 2014). The aggregate content, grading, shape and surface texture influence workability, packing density, strength and dimensional stability of concrete. Therefore, quantitative analysis of mix composition is occasionally required to check for compliance with specifications, establish the quality of the hardened concrete or to determine the causes of degradation (The Concrete Society, 2014, Poole and Sims, 2016) and assess future performance. Every so often, disputes arise over the actual composition of concrete, especially when a structure fails to perform to expectations.

There are several methods available for determining the composition of cement paste. Examples include the physicochemical method of BS 1881-124 (British Standards Institution, 2015) and petrographic methods such as fluorescence microscopy (Mayfield, 1990, Elsen et al., 1995, Sibbick et al., 2019) and backscattered electron microscopy (BSE) (Wong and Buenfeld, 2009, Wong et al., 2013, Yio et al., 2014). A recent round-robin assessment involving eleven laboratories in Europe (Wong et al., 2020) has demonstrated the viability of petrographic microscopy methods for determining w/c ratio in hardened concrete. The aggregate content and particle size grading can be determined by

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breaking down the cementitious matrix through mechanical, thermal or chemical (acid dissolution) treatments, followed by a sieve analysis of the remaining material (British Standards Institution, 2015). However, this approach is laborious and prone to errors (The Concrete Society, 2014) especially when the aggregate contains acid-soluble phases. Another method is based on petrographic examination (French, 1991, The Concrete Society, 2010, ASTM International, 2019a, ASTM International, 2020) of a random cross-section, followed by quantitative stereology or image analysis (Mertens and Elsen, 2006) to obtain the volume fractions of the aggregate and cement paste. Then, the mass proportions can be calculated from the phase densities (Applied Petrography Group, 2010). This method, also known as micrometric or modal analysis, offers some advantages over the physicochemical method. Nevertheless, there have been no comprehensive precision experiments to evaluate the accuracy and precision of these methods (The Concrete Society, 2014).

Several researchers (Dequiedt et al., 2001, Ozen and Guler, 2014, Boschmann Käthler et al., 2017) have used desktop flatbed scanners to image and quantify aggregate particles in concrete. This method requires the sample surface to be polished and stained to enhance the contrast between aggregate particles and cement paste for image analysis. Furthermore, the spatial resolution of flatbed scanners is not sufficient to resolve fine aggregate particles. BSE microscopy combined with energy dispersive X-ray spectroscopy (EDS) offers a high resolution technique to extract aggregate particles from concrete (Head and Buenfeld, 2006). However, due to the very small field of view of BSE microscopy, a large number of images is required to ensure sampling representativeness. More recently, X-ray microtomography (μ CT) has been employed to characterise aggregate particles (Mendes et al., 2009, Thomas et al., 2018, Estephane et al., 2019, Sokhansefat et al., 2019). While this method is non-destructive and requires minimal sample preparation, its spatial resolution is insufficient to detect fine aggregate particles in a representative volume of concrete. The contrast between fine aggregate particles and cement paste is too low due to poor differential X-ray absorption (Mac et al., 2021).

Micro X-ray fluorescence (μ XRF) is a non-destructive microscopy technique which allows elemental mapping of multiphase materials at microscale. This technique has been used to study chloride transport (Davis et al., 2011, Alzyoud et al., 2016, Khanzadeh Moradillo et al., 2017, Olsson et al., 2018, Maraghechi et al., 2018) and carbonation (De Weerd et al., 2019) in mortars and concretes. μ XRF has higher spatial resolution than flatbed scanners or μ CT. Furthermore, it is able to scan a much larger area than SEM-EDS within a shorter time. This provides the possibility to map a large area of concrete to produce high resolution composite element maps of cement paste and aggregate particles. These element maps can then be used to differentiate various phases in concrete by means of image analysis. The idea is similar to the BSE-EDS method proposed by (Head and Buenfeld, 2006) whereby various element maps of aggregates are combined to facilitate image analysis of aggregates.

This paper aims to investigate the feasibility of μ XRF for determining the cement paste and aggregate content in hardened concrete. A parametric study was conducted to determine the optimal operating conditions of μ XRF for elemental mapping of concrete. A new image analysis procedure was then proposed to extract aggregate particles from the element maps acquired with μ XRF. The method was tested on five mixes containing different types and contents of aggregates including gravel, limestone and synthetic lightweight aggregates. The results were compared and verified against the actual mix design and results from point-counting analysis. Segmented aggregates were further quantified

for particle size distribution, aspect ratio and orientation. The advantages and limitations of the method and its applicability to other types of concrete are discussed. The outcome of this study is expected to contribute to the development of a standardised robust method for estimating concrete composition through large-area elemental mapping.

2 Experimental

2.1 Materials and sample preparation

Five concretes with different types of coarse and fine aggregates were prepared according to the mix proportions in Table 1, calculated using the absolute volume method. Ordinary Portland cement CEM I, with oxide composition of 65.0% CaO, 20.5% SiO₂, 5.0% Al₂O₃, 2.7% Fe₂O₃, 0.9% MgO, 0.19% Na₂O, 0.73% K₂O, 3.1% SO₃, and < 0.01% Cl was used as the main binder. The specific gravity, Blaine specific surface and loss on ignition were 3.15, 342 m²/kg and 1.36% respectively. The aggregates used were siliceous sand, crushed limestone, Thames Valley gravel and sintered lightweight aggregates (Lytag) produced from pulverised fuel ash. The specific gravity, water absorption and moisture content of the aggregates are given in Table 2 whereas the particle size distributions (PSDs) are shown in Fig. 1. The water/cement (w/c) ratio was kept at 0.5. The total aggregate volume fraction ranged from 68 to 72% and the fine-to-coarse aggregate mass ratio varied from 0.54 to 1.05. Tap water was used as batch water, adjusted to account for aggregate absorption.

For each mix, a cylindrical sample of 100 Ø × 50 mm was prepared. Cement and aggregates were dry mixed for around 30 s prior to the addition of water for further wet mixing of 3 min in a Hobart mixer. The fresh concrete mix was then placed in the cylindrical steel mould and compacted in three layers on a vibrating table. For samples LS-1, LW-1 and LW-2, a rebar of 10 mm Ø was embedded at a cover depth of 10 mm to investigate its influence on analysis. All mixes were compactable with no sign of bleeding and segregation. Immediately after casting, the samples were covered with wet hessian and plastic sheet for 24 h. Following that, the samples were demoulded and cured in a fog room at 98% RH and 21°C for 28 d. After curing, a 100 mm × 50 mm × 10 mm slice was sectioned vertically from the centre of each sample with a diamond abrasive cutting machine for analysis. The surface of the cross-section was patted dry with a paper towel and then left to dry in air (~45% RH, 21°C) until constant mass. No further sample preparation was required.

2.2 Micro XRF

The µXRF used in this study was an EDAX Orbis PC analyser equipped with a 50 kV Rh anode X-ray tube and an 80 mm² Si(Li) energy-dispersive detector with a Be window capable of analysing elements from Na (Z=11) to U (Z=92). The analyser features monolithic polycapillary focusing optics and automated brass collimators that can produce X-ray beam spot sizes of 30 µm, 1 mm and 2 mm, respectively. The system has a motorised XYZ stage with 5 µm minimum step size, 100 × 100 × 100 mm stage travel, and video cameras (10x and 70x) to allow precise location of regions of interest and large area mapping. The analysis chamber can be operated under vacuum or ambient conditions and can accommodate samples up to 270 × 270 × 100 mm. Control of the system and data collection were performed using ORBIS Vision (v.2.0). The collected spectra were analysed to identify the characteristic X-ray element peaks. Escape peaks were subtracted from the main spectrum, while Rayleigh Rh L peak was removed by means of a thin 25 µm Al filter.

2.3 Parametric study to optimise elemental mapping

There are several operating parameters that can influence μ XRF mapping and these should be optimised for specific application. For example, the beam spot size determines the sample area irradiated by the X-ray beam and therefore the spatial resolution of the element maps. Beam voltage controls the acceleration of electrons towards the Rh target anode which in turn affects the energy of the excitation X-rays and the detectable elements. Beam current determines the amount of electrons available for exciting the Rh target and in turn the intensity of the X-ray beam produced. A high beam current increases the dead time of the detector, resulting in a higher percentage of incoming pulses being rejected. The recommended dead time is between 30 and 50% (EDAX Ametek Inc., 2009), and exceeding this range produces an artificial pile up or sum peak.

Time constant (also known as amplifier time) is the amount of time taken to process each photon entering the detector. A shorter amplifier time would result in a higher count rate of photons and total detected signal, but at a risk of lower accuracy in the assigned energy channels. Dwell time is the amount of time the X-ray beam spends on a particular point. A higher dwell time would improve the signal-to-noise ratio and the detection of elements with lower emission signals (e.g. trace elements), but this comes at a cost of longer mapping time. Further details of these parameters are provided in (Abdul Wahid, 2017, Haschke, 2014).

A parametric study was conducted to determine the optimal μ XRF operating conditions to achieve high signal-to-noise ratio and high contrast element maps for image analysis. The main parameters investigated were beam spot size (30 μ m, 1 mm, 2mm), beam voltage (10, 20, 30, 40, 50 kV), time constant (1.6, 3.2, 6.4, 12.8 μ s) and dwell time (30, 50, 100, 200, 300, 400 ms). The optimisation was carried out by varying the main parameter and keeping other parameters fixed at beam spot size of 30 μ m, beam voltage of 25 kV, beam current of 100 μ A, time constant of 12.8 μ s and dwell time of 100 ms. The parametric study was carried out on a randomly selected area of 11.4 $\times$ 8.9 mm² from sample Ls-1, scanned at a pixel spacing of $\sim$ 45 μ m.

For the final analysis, the entire sample cross-section ($\sim$ 100 $\times$ 50 mm²) was scanned at a pixel spacing of $\sim$ 90 μ m to produce a large area composite element map. In total, over 12 element maps were captured and analysed for each sample. All data collection was performed under vacuum ($\sim$ 0.4 Torr) to minimise the loss of fluorescence intensity to absorption by atmospheric gas molecules.

3 Image analysis

3.1 Proposed method

An overview of the proposed method for segmenting the aggregate and cement paste fraction from the large area element maps is presented in the flow chart shown in Fig. 2. An example application of the proposed method on sample TVG is illustrated in Fig. 3. The first step involves identifying the main and trace elements present to make sure all aggregates are captured and adequately represented for subsequent image analysis. For instance, siliceous sand contains mainly Si, limestone aggregate contains mainly Ca and Mg, whereas Thames Valley aggregate contains not only Si but also Fe and Al. Lytag lightweight aggregates contain a variety of elements including Fe, Si, S and Mg.

Once these elements are identified, the first composite map is created from Si and other relevant elements, but excluding Ca to extract all non-Ca containing phases (Fig. 3b). This is performed by mathematically adding the Si map and other relevant element maps in Fiji (Schindelin et al., 2012). This creates a good contrast between aggregate particles and cement paste as seen in Fig. 3b. The composite image is then subtracted from the Ca map to create a second composite image with a pixel value of zero for all non-Ca containing phases (Fig. 3c). These phases can then be segmented easily by applying a threshold at zero on the image histogram (Fig. 3d).

For concretes containing siliceous and lightweight aggregates, the steps above would extract all aggregates including sand. In case some aggregate particles are excluded, a suitable element map with a distinct histogram peak for the missing particles can be segmented separately (Fig. 3e) and added to yield a total aggregate binary image (Fig. 3f). The coarse aggregate can then be separated from the fine aggregate by means of size discrimination based on the particles' Feret diameter using 'Analyze Particles' in Fiji. All particles greater than 5 mm are classified as coarse whereas those smaller than this value are classified as fine (Neville, 2011) (Fig. 3g-h).

For concretes containing crushed limestone, only the fine aggregate (i.e. sand) would be extracted by the segmentation step above. In order to extract limestone aggregate, the Ca map can be added to the Mg and if necessary Fe and Ni maps to produce a separate composite image. The histogram of this image would exhibit two distinct peaks corresponding to the cement paste and limestone aggregate respectively. The distinct peaks enable a straightforward segmentation using the minimum between peaks as the threshold. This would yield a binary image of the coarse limestone aggregate. Following segmentation, noise is removed by morphological operations in the order of erosion, dilation and hole-filling. If a rebar is present, it is removed by tracing and subtracting the binary image of the Fe map.

The segmented area of the fine and coarse aggregate are then divided by the total image area (excluding rebar) to calculate the volume fractions of the two phases (Underwood, 1970, Russ and Dehoff, 2000). The volume fraction of cement paste is taken as the complement of the total volume fraction of fine and coarse aggregates. Any entrapped air voids are treated as part of the cement paste. The results are compared and validated with those obtained by direct point counting and data from the original mix design.

3.2 Point counting

Point counting (also known as micrometric or modal analysis) was performed by overlaying a grid of ~2000 equally spaced points (ASTM International, 2019b) on a separate composite image, obtained by combining all element maps. The composite image showed good contrast between different phases and this facilitated point-counting. The phase underlying each grid point was identified based on its size, shape and element composition. If any uncertainty arises with the identification, then additional μ XRF spot analysis was carried out on individual element maps to confirm the underlying phase. It should be noted that the point counting was done manually, and as such it was a very tedious and time consuming process, but should yield an accurate estimate of the phase composition.

Three phases were identified and tallied: coarse aggregate, fine aggregate and cement paste. Coarse aggregate particles can be easily distinguished based on their large size, clear boundaries and defined element composition. Fine aggregate tends to appear as individual particles consisting mainly of Si whereas cement paste appears as a continuous matrix consisting mainly of Ca. These allow good discrimination between coarse and fine aggregate particles, and

176 cement paste. Grid points which fell on the borders were counted as half a point to avoid introducing bias towards the
177 results. The total number of grid points falling on a particular phase was divided by the total number of points counted
178 to calculate the volume fraction of that phase (Underwood, 1970, Russ and Dehoff, 2000).

179 3.3 Quantification of aggregate characteristics

180 The binary images of coarse and fine aggregates obtained in Section 3.1 were further analysed to quantify various
181 parameters including particle size, aspect ratio and orientation. Prior to analysis, the images of fine aggregate were
182 subjected to watershed segmentation to separate touching particles. This step was not necessary for coarse aggregate
183 particles as they were already separated. Particle size was taken as the average between the minimum and maximum
184 Feret diameters. Particle aspect ratio was taken as the ratio of the minimum to maximum Feret diameters, where a
185 value close to 1 represents a highly circular particle whereas a value close to 0 represents an elongated particle.
186 Orientation was taken as the angle between the maximum Feret diameter and the x-axis of the image (perpendicular to
187 the casting direction), ranging from 0 to 90°. All measurements were performed using the 'Analyze Particles' function in
188 Fiji, with any particles on the image edges excluded. The number of coarse and fine aggregate particles analysed per
189 sample were in the ranges of 64 to 241 and 4945 to 6093 respectively.

190 4 Results

191 4.1 Optimisation of micro XRF for elemental mapping

192 Fig. 4 shows the effect of beam spot size, beam voltage, time constant and dwell time on the quality of element maps,
193 supported by image greyscale intensity profiles drawn across lines A-A and B-B, presented in Fig. 5. As expected, the
194 image resolution increases with decreasing beam spot size. The highest spatial resolution was achieved with a beam
195 spot size of 30 µm, sufficient to resolve both fine and coarse aggregate particles. The intensity profiles (Fig. 5a) show
196 that as the beam spot size decreases, the greyscale variation across the aggregate particle becomes more distinct and
197 contrasted from the surrounding background. The improvement can be attributed to the combined effect of a finer
198 beam spot size and higher-intensity X-rays formed by the polycapillary optics.

199 The applied beam voltage needs to be higher than the electron-binding energy (k-edge adsorption) of a particular
200 element in order to produce fluorescence emission. The effect of beam voltage is less significant since most elements in
201 concrete have electron-binding energies less than 10 keV and are therefore detectable at the lowest applied voltage
202 (Fig. 5b). However, for certain heavy elements with high binding energies, the effect of beam voltage can become
203 noticeable. For example, the Fe map (Fig. 4) exhibits better contrast with increasing beam voltage due to more signals
204 being generated, but at a cost of a larger X-ray sampling volume.

205 The effect of time constant varies depending on the amount and type of elements present. For elements which are
206 abundant (e.g. Ca and Si), the time constant does not seem to have an effect on the map quality. For less abundant
207 elements such as Fe, the map quality improves with time constant due to increased spectral resolution. However, if the
208 element has an X-ray energy peak very close to that of an abundant element (e.g. Al and Si), the map intensity may
209 appear misleadingly better at a lower time constant due to inaccurate energy channel assignment (Fig. 4 & 5c). In
210 contrast, the dwell time has a monotonic effect on all elements. The longer the dwell time, the clearer the image due to

a higher amount of X-ray photons detected (Fig. 4 & 5d). This effect is most pronounced on trace elements e.g. Mn. However, the use of large time constant or dwell time will incur a penalty of long mapping session, which is impractical for routine large area analyses of concrete samples.

In view of the findings above and the need to strike a good balance between data quality and practicality, it was concluded that the optimal settings for μ XRF elemental mapping of concrete are a beam spot size of 30 μ m, a beam voltage of 25 kV, a time constant of 25.6 μ s and a dwell time of 100 ms. These settings were adopted for all subsequent mapping. The beam current was adjusted correspondingly to achieve a dead time of 40% across all samples.

4.2 Measured aggregate and cement paste contents

Table 3 presents the volume fractions of fine aggregate, coarse aggregate and cement paste measured by the proposed method (μ XRF) and point-counting. As expected, the volume fractions of coarse aggregate were the highest, followed by those of fine aggregate and cement paste, consistent across all samples and between the two methods. The volume fractions were converted to kg/m³ using the known specific gravities of the mix constituents (Table 2). The measured fine and coarse aggregate contents were then used to compute the fine-to-coarse aggregate (f/c) ratio. The cement paste content was further deconvolved into cement and water contents using the known w/c ratio.

Fig. 6a-b plot the measured values against the actual values for all samples. Eighty-seven percent of the measured values of the fine, coarse and total aggregate contents fell within $\pm 12\%$ of the actual values. The measured f/c ratios, however, showed larger deviations. This could be due to misclassification of the fine and coarse aggregate particles (see Discussion). The measured values for cement paste were all within $\pm 12\%$ of the actual values, except for one mix (i.e. Lw-1) due to underestimation of the total aggregate content. It is worth noting that there was no consistent under or overestimation, confirming that no systematic errors were introduced. Fig. 6c-d shows that the results obtained with the proposed μ XRF method were in good agreement with those from point counting, with all values falling within $\pm 4\%$.

Fig. 7a presents the maximum and average errors for the aggregate and cement paste contents, and f/c ratio measured by both methods for all mixes. Here, the errors refer to the difference between measured and actual values, expressed as a percentage of the actual value. The average errors for the fine aggregate, coarse aggregate, total aggregate and cement paste contents, and f/c ratio measured by both methods were 12%, 12%, 3.4%, 10%, and 27% respectively. Due to a larger population size, the average errors for the total aggregate content were smaller than those of the fine and coarse aggregate contents measured separately.

Fig. 7b presents the frequency and cumulative distribution of errors from all measured values of fine aggregate, coarse aggregate and cement paste contents. The plot shows both the proposed μ XRF method and point counting gave very similar distribution of errors, with 40% and 80% of the measured values within 8% and 20% of the actual values respectively.

4.3 Particle size distribution, aspect ratio & orientation

Fig. 8 compares the measured particle size distributions (cumulative area fraction vs. particle size) obtained from image analysis of μ XRF element maps against the 'actual' PSDs from sieve analysis. Overall, the PSDs of coarse aggregates appear to be slightly underestimated, especially for the Lytag particles. In contrast, the PSDs for the fine aggregates

were in excellent agreement with sieve analysis. It is expected that analysing more particles from different cross-sections will improve the results. Unlike sieve analysis which measures particles in their preferred orientation along the axis of the minimum projected area, image analysis takes into account the shape of particles and measures them in a random orientation. Therefore, image analysis is often deemed more accurate and reliable than sieve analysis, provided that a sufficient number of particles are analysed (Fernlund et al., 2007).

Fig. 9 shows the measured aspect ratio of the coarse and fine aggregate particles. As expected, coarse Lytag aggregates, which are generally spherical, exhibited aspect ratios close to unity, whereas gravel and limestone particles exhibited lower aspect ratios due to their more irregular shapes. By contrast, all fine aggregates exhibited very similar distributions of aspect ratio, with 50% of the population being higher than 0.6. The orientation of the coarse aggregate particles is shown in Fig. 10. Most aggregate particles were orientated between 30° and 60° relative to the casting surface. This indicates that the compaction process did not induce preferred alignment of the particles to the mould.

4.4 Effect of image size and spatial variability

In order to investigate the effect of element map size on the measured aggregate and cement paste contents, the main binary images were subdivided into ~35 images of 110 mm², 20 images of 230 mm², 10 images of 430 mm², 8 images of 580 mm², 4 images of 1100 mm², 3 images of 1400 mm² and 2 images of 2200 mm² for analysis. The measured contents were then normalised to those obtained from the entire image, acting as benchmarks. Fig. 11 shows the maximum and minimum values observed as a function of increasing image size. As expected, the accuracy in the measured aggregate and cement paste contents improved with increasing image size. The largest variability is observed when the image size is <500 mm² (~22 mm x 22 mm), which is of the same order as the maximum aggregate size. Clearly, this is insufficient to capture a representative number of aggregate particles for analysis.

The spatial distribution was further quantified by calculating the coefficient of variation (COV) of the measured contents from the subsampled 110 cm² images and correlated with the relative errors of each phase measured in Section 4.2. Fig. 12 shows that the errors reduced with the coefficient of variation, irrespective of the phases measured, indicating that accuracy of the measurement improves with the homogeneity of phases. Overall, an image size of > 2000 mm² (~45 mm x 45 mm) is considered to be sufficient to obtain representative results, as indicated by the convergence of the measured values to within ±10% of the benchmarks. This equates to an image length of at least five times the maximum aggregate size. It should be noted that only one cross section was analysed for each sample in this study, and therefore testing replicates is expected to further improve the accuracy of the results.

5 Discussion

This study demonstrated the feasibility of µXRF combined with image analysis for determining the aggregate and cement paste contents in concrete. Unlike other methods which require colour staining, epoxy impregnation, grinding and polishing (Head and Buenfeld, 2006, Ozen and Guler, 2014, Boschmann Käthler et al., 2017), µXRF requires minimal sample preparation and therefore is useful for routine analysis. In comparison with SEM-EDS, µXRF is capable of large-area mapping (100 × 100 mm²) without the need for acquiring and stitching a large number of montage images which can be both time-consuming and error-prone. In comparison with a flatbed scanner, µXRF offers high spatial resolution and contrast element maps which enable accurate measurement of fine and coarse aggregates, and cement paste. It

should be pointed out that μ XRF mapping can be time consuming depending on the map area and instrument used. In this study, the average time taken to scan an area of $\sim 100 \times 50 \text{ mm}^2$ with the Si(Li) detector at optimised settings was around 2 d. It is anticipated with the newer silicon drift detector (SDD), which is able to collect X-rays at two orders of magnitude faster (Strüder et al., 2020), the total mapping time can be significantly reduced.

The good agreement between the proposed image analysis procedure and point-counting shows that the proposed method is valid and reliable. Unlike point-counting, the proposed method does not require manual identification of the phases, which can be time consuming, laborious and requires trained operators to reduce errors. The average time required to analyse a sample using the proposed method is approximately 30 min, as opposed to several hours by point-counting. Due to the finite resolution of μ XRF, some smaller particles may be excluded from analysis leading to an underestimation of aggregate contents. Assuming that the smallest resolvable particle size is around 3 pixels, which is equal to 0.27 mm ($3 \times 90 \mu\text{m}$), around 10 vol. % of the fine aggregate particles may be excluded (estimated from sieve analysis, Fig. 1). However, some noise that remains following morphological operations may contribute erroneously to the fine aggregate content.

Coarse aggregate particles which exhibit large grey level variations may be under-segmented by the proposed method due to some parts of the particles not falling within the threshold range. This can be overcome to some extent by combining multiple element maps (Fig. 3b) to ensure that the particles are fully segmented. Coarse aggregate particles which are sectioned across their tips may lead to an under-estimation of size and misclassification of the aggregates. This is particularly an issue where fine and coarse aggregates share similar composition and are indistinguishable from the element maps.

The proposed method requires the specific gravities of aggregates and cement to be known. This is however not a limitation given that the specific gravities of most types of aggregate and cement used in concrete are already available. Therefore, so long as the raw material types can be determined (e.g. from the element composition), the specific gravities can be established. The specific gravity of Portland cement does not vary significantly and can be taken as 3.15 (Yio et al., 2014). For multi-component cements containing supplementary cementitious materials (SCMs), additional analyses such as those presented in (Deschner et al., 2013, Yio et al., 2014) will be required to determine their replacement levels.

It is envisaged that the method can be applied to concretes containing SCMs, entrained air voids and foreign objects (e.g. reinforcing steel). SCMs such as silica fume, slag and fly ash share common elements to those already present in conventional concrete and should not complicate the image analysis. Furthermore, these SCMs are much smaller in particle size than those of fine aggregate. Air voids can be filled with a suitable medium such as gypsum (Gudmundsson et al., 1979) or talcum powder (Wong et al., 2015) to provide a flat surface for analysis. Any cavities (or protuberances) present on the surface may absorb the fluorescence emitted by the underlying phase, causing inaccuracies in the element maps. Filled air voids can be removed from the image based on their spherical shape and known filler composition. Foreign objects such as rebar and spacer in a concrete can be removed by either manual tracing or by subtracting binary images of the relevant element maps (e.g. Fe for rebar).

When applying the proposed method on real structures, it is important to be wary of sampling concretes that have been affected by segregation or severe degradation. If there is segregation, the spatial distribution of the aggregate particles will no longer be homogenous and this will lead to an inaccurate estimation of the overall mix composition, unless the purpose of the analysis is to establish evidence of segregation. As always, sampling from several locations/levels in a structure will improve overall representativeness. It is also important that the samples are free from severe chemical deterioration e.g. sulphate attack and alkali-aggregate reaction, that would alter the composition of the cement paste and aggregate particles.

6 Conclusions

This study investigated the feasibility of using μ XRF for measuring cement paste and aggregate content in hardened concrete through large-area composite element mapping. A parametric study was carried out to determine the optimal settings for elemental mapping of concrete with μ XRF. A new image analysis procedure was then developed to segment aggregate particles from composite images of element maps. The method was tested on five concrete mixes containing different types of aggregates including gravel, limestone, siliceous sand and sintered lightweight aggregates. Over 12 element maps ($100 \times 50 \text{ mm}^2$) per sample were obtained and analysed. The results were compared against point-count analysis and data from the actual mix design. The segmented aggregate particles were further analysed for grading (size distribution), aspect ratio and orientation. The key findings are:

- a. The parametric study showed that a $30 \mu\text{m}$ beam spot size, 25 kV beam voltage, 25.6 μs time constant and 100 ms dwell time of 100 ms are optimal for elemental mapping of concrete with μ XRF. These settings enable the acquisition of high resolution and high contrast large-area element maps suitable for image analysis.
- b. The average errors for the measured fine aggregate, coarse aggregate, total aggregate, cement paste contents and fine-to-coarse aggregate ratio with the proposed μ XRF method were 12%, 12%, 3.4%, 10%, and 27% respectively. Eighty-seven percent of the measured values of fine, coarse and total aggregate contents fell within $\pm 12\%$ of the actual values.
- c. All values measured with the proposed μ XRF method fell within $\pm 4\%$ of those from point-count analysis. This confirms the validity and reliability of the μ XRF method. Unlike point counting, the proposed method does not require manual identification of the phases, which can be time consuming, laborious and requires trained operators to reduce human errors.
- d. The particle size distribution (PSD) of coarse aggregates measured from image analysis were slightly underestimated, possibly due to the low number of particles sampled. The PSDs of fine aggregates agreed well with sieve analysis. Coarse Lytag aggregates exhibited aspect ratios close to unity (rounder), whereas gravel and limestone particles exhibited lower aspect ratios (more elongated). Most coarse aggregate particles were orientated between 30° and 60° relative to the casting surface.
- e. The accuracy of the measured aggregate and cement paste contents improved with increasing image size and with the homogeneity of the measured phases. Overall, an image size of $> 2000 \text{ mm}^2$ ($\sim 45 \text{ mm} \times 45 \text{ mm}$) is sufficient to obtain good results. This equates to an image length of at least five times the maximum aggregate size.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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Analysis of cement paste and aggregate content of concrete using micro X-ray fluorescence

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Table 1 Mix proportions.

Mix ID*	CEM I (kg/m ³)	Water (kg/m ³)	w/c (-)	Limestone (kg/m ³)	Gravel (kg/m ³)	Lytag (kg/m ³)			Sand (kg/m ³)	Aggregate volume fraction (%)	f/c† (-)
						8/12	4/8	0/4			
Ls-1	350	175	0.5	1160	-	-	-	-	740	71.5	0.64
Ls-2	375	188	0.5	1077	-	-	-	-	718	68.0	0.67
TVG	365	207	0.5	-	1167	-	-	-	628	70.0	0.54
Lw-1	350	175	0.5	-	-	142	563	-	740	70.0	1.05
Lw-2	350	175	0.5	-	-	142	563	472	-	71.4	0.67

* Ls = crushed limestone aggregate, TVG = Thames Valley gravel, Lw = light-weight aggregate (Lytag)

† f/c = fine/coarse aggregate mass ratio

Table 2 Properties of aggregates.

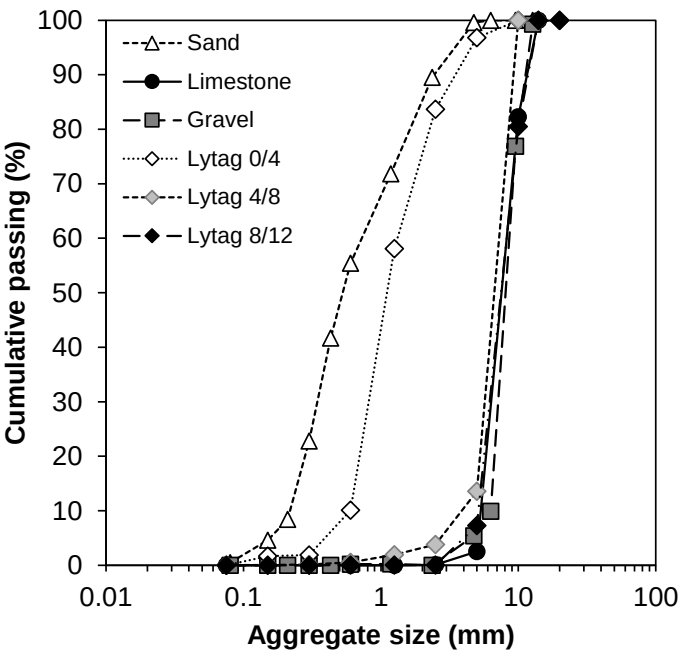
Aggregate type	Maximum aggregate size (mm)	Specific gravity	24-h absorption (%)	Moisture content (%)
Limestone	10	2.71	0.88	0.46
Gravel	13	2.53	0.84	0.42
Lytag 8/12	14	1.65	24.0	-
Lytag 4/8	10	1.64	27.9	-
Lytag 0/4	5	1.65	3.70	-
Sand	5	2.60	0.62	0.25

Table 3 Measured volume fractions (%) of fine aggregate, coarse aggregate and their total, and cement paste.

Sample	Fine aggregate			Coarse aggregate			Total aggregate			Cement paste		
	Mix design	μXRF	Point-count	Mix design	μXRF	Point-count	Mix design	μXRF	Point-count	Mix design	μXRF	Point-count
Ls-1	28.5	23.0	22.6	43.0	45.0	46.0	71.4	68.0	68.6	28.6	32.0	31.4
Ls-2	28.3	31.4	32.2	39.7	34.8	35.3	68.0	66.3	67.5	32.0	33.7	32.5
TVG	23.9	22.6	22.0	46.1	48.6	48.9	70.0	71.2	70.9	30.0	28.8	29.1
Lw-1	28.5	32.4	30.9	43.0	30.8	30.9	71.5	63.2	61.8	28.6	36.8	38.2
Lw-2	28.5	31.3	30.5	43.0	39.6	39.4	71.5	70.8	69.9	28.6	29.2	30.1

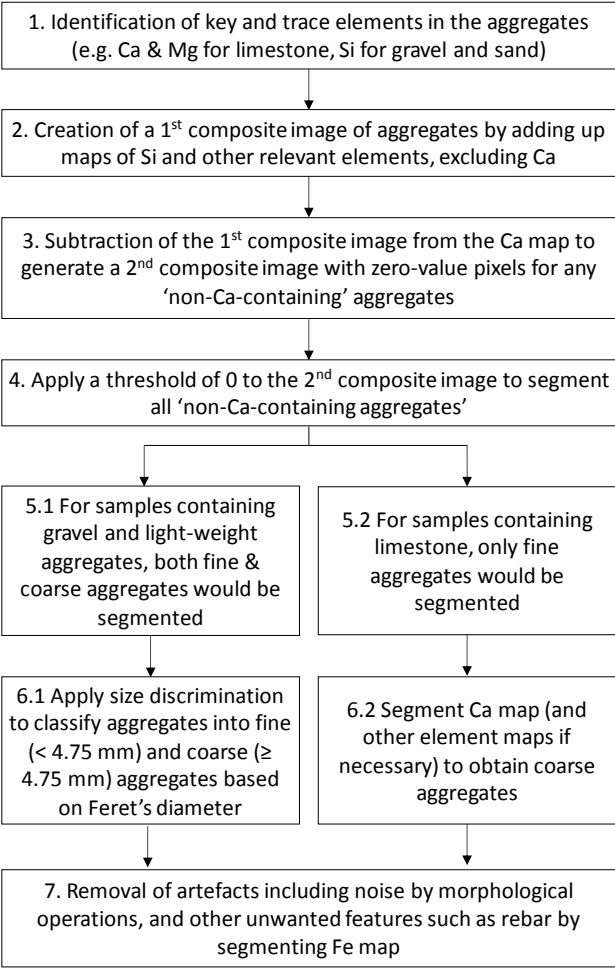
¹ Corresponding author. E-mail: hong.wong@imperial.ac.uk Telephone: +44 (0)20 7594 5956

466 Fig. 1 Particle size distribution of aggregates from sieve analysis.



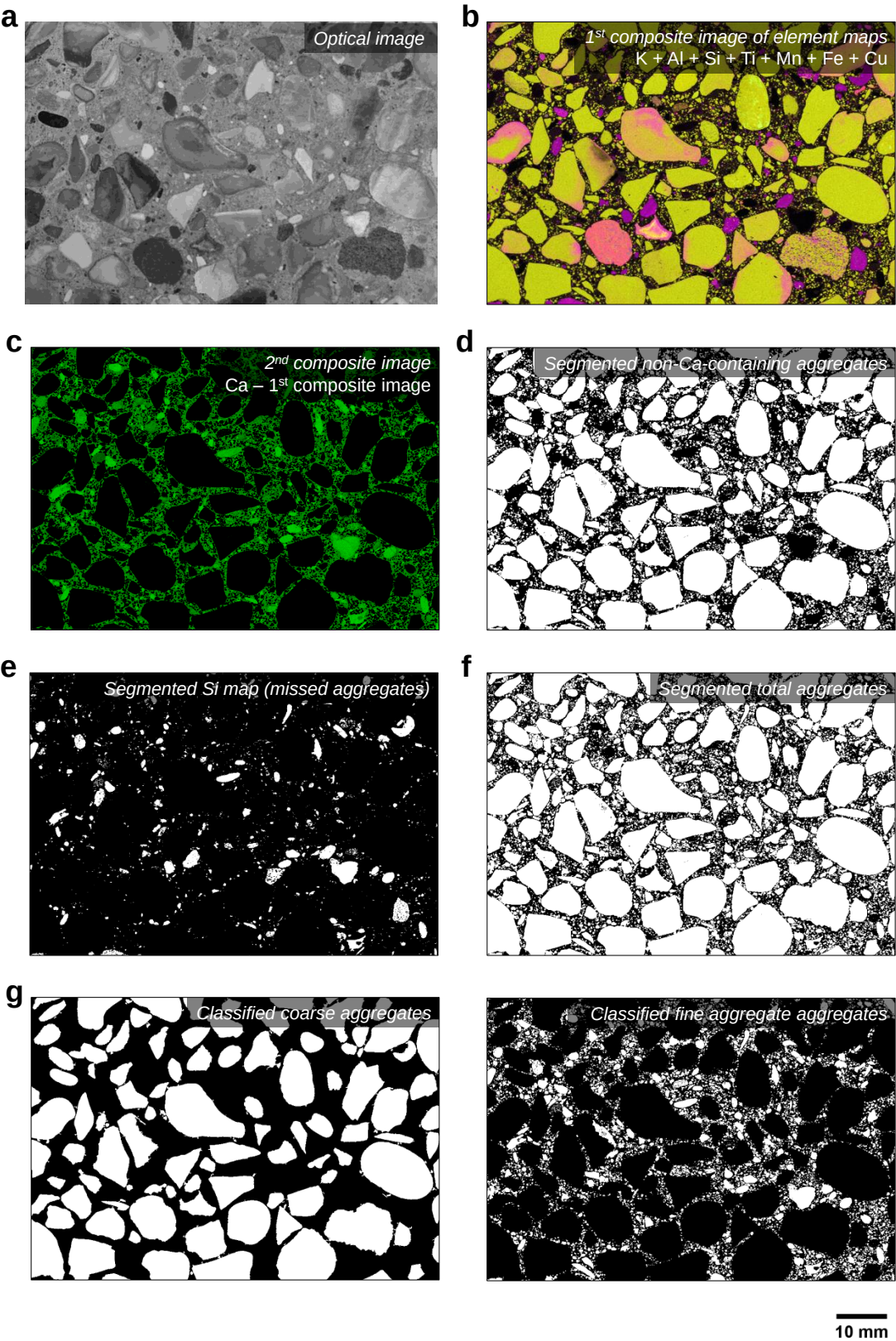
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468 **Fig. 2 Overview of the proposed image analysis procedure for extracting fine and coarse aggregate particles from**
469 **large-area element maps acquired with μ XRF.**

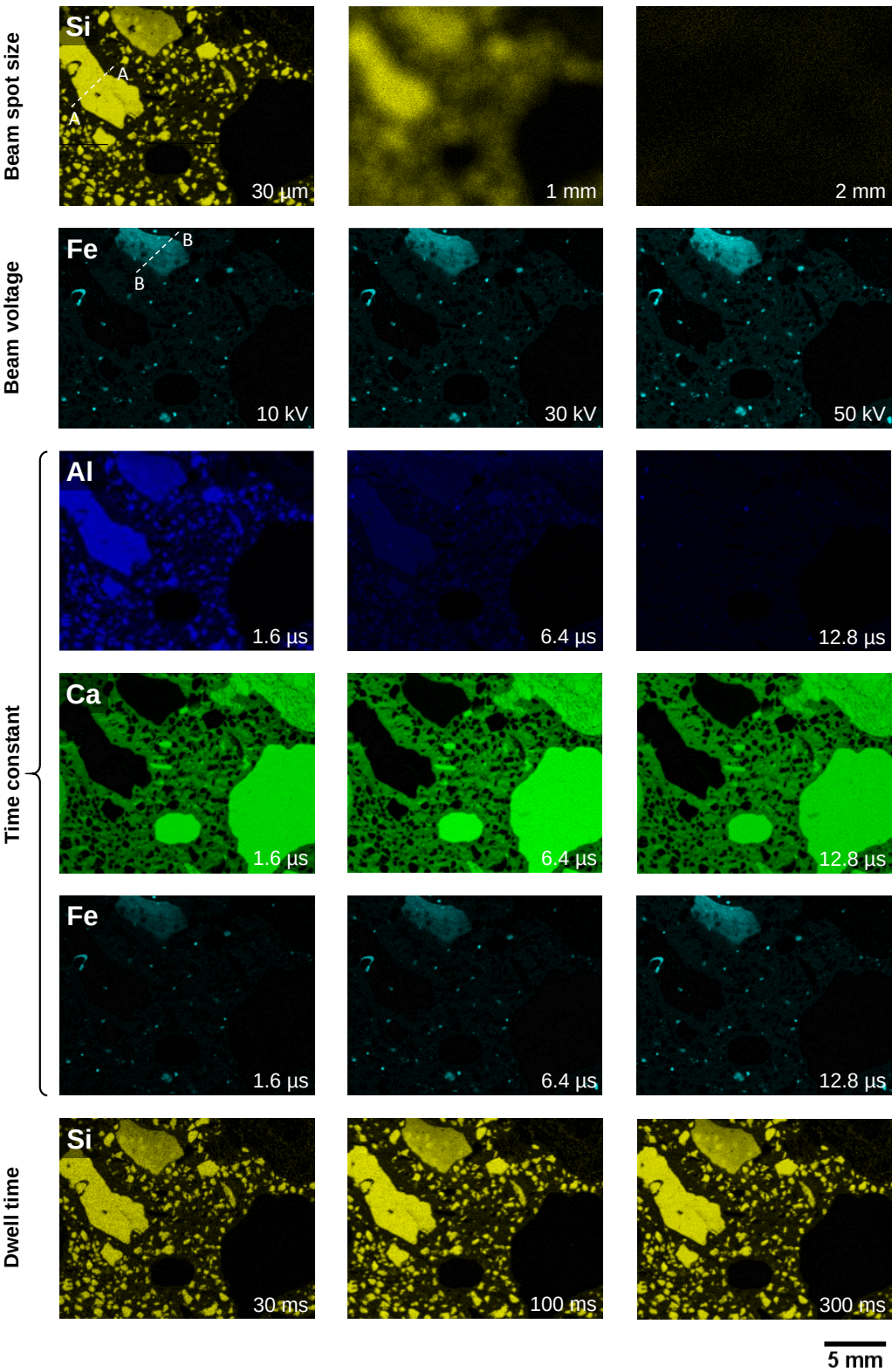


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471 Fig. 3 Example application of the proposed image analysis procedure on sample TVG.

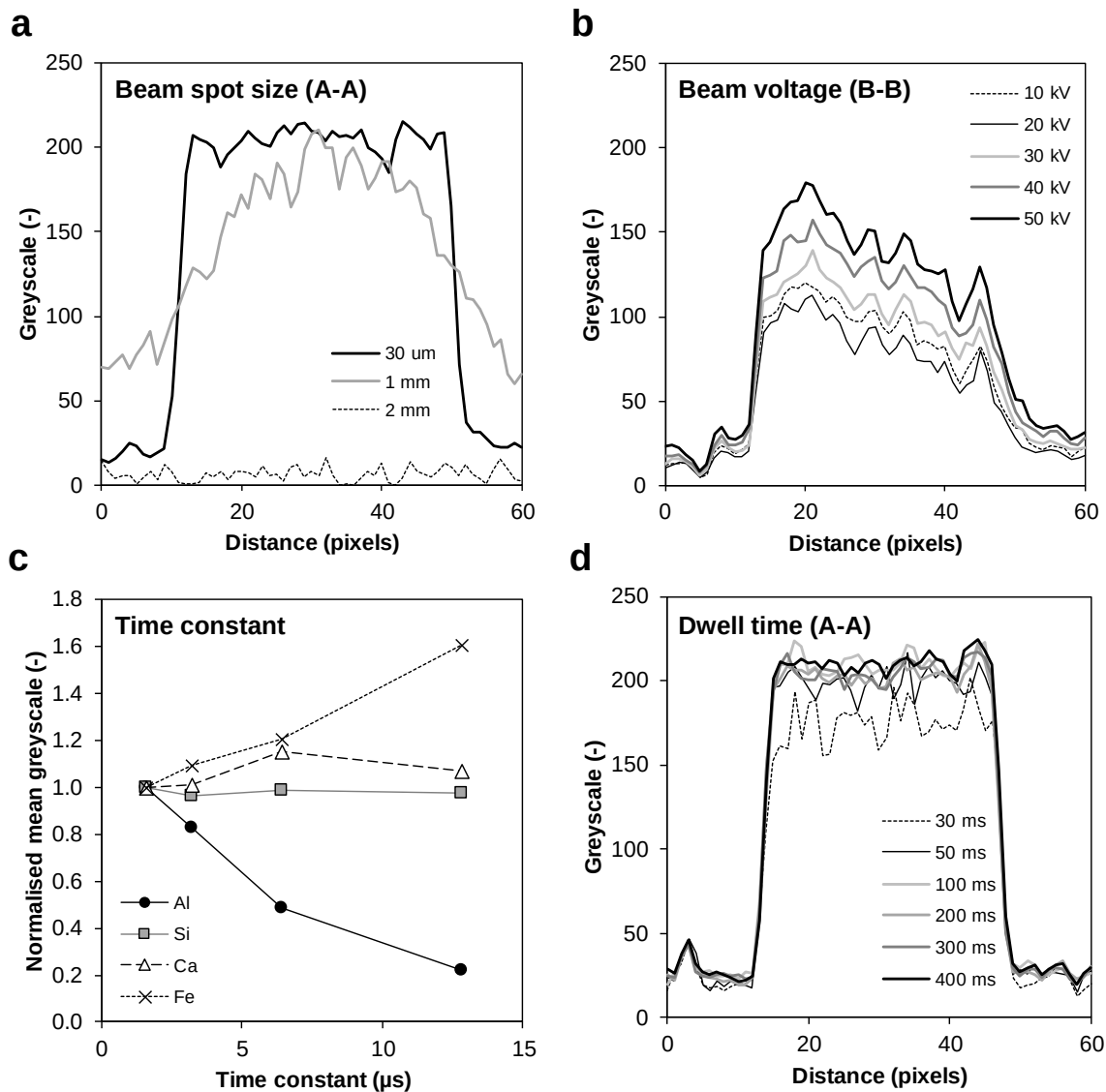


472 Fig. 4 Effect of X-ray beam spot size, beam voltage, time constant and dwell time on elemental mapping.



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474 Fig. 5 Effect of X-ray beam spot size (a), beam voltage (b), dwell time (d) and time constant (c) on image signals.



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Fig. 6 Comparison between measured and actual values of aggregate content, cement paste content, and fine/coarse aggregate (f/c) ratio (a-b); Comparison of measurements obtained with the proposed method (μ XRF) and point counting (ptc) (c-d). Dash lines represent $\pm 10\%$ of actual values.

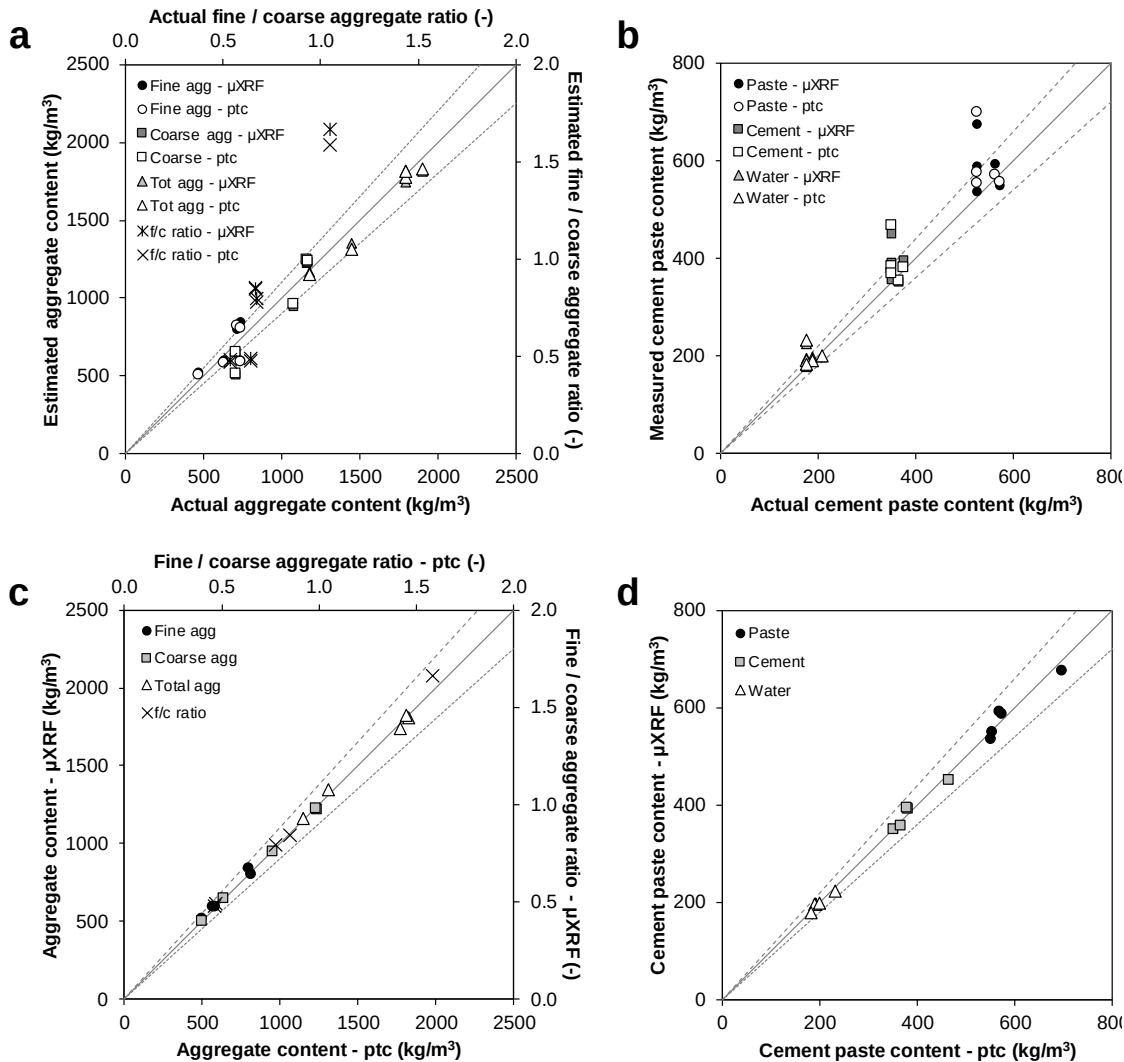
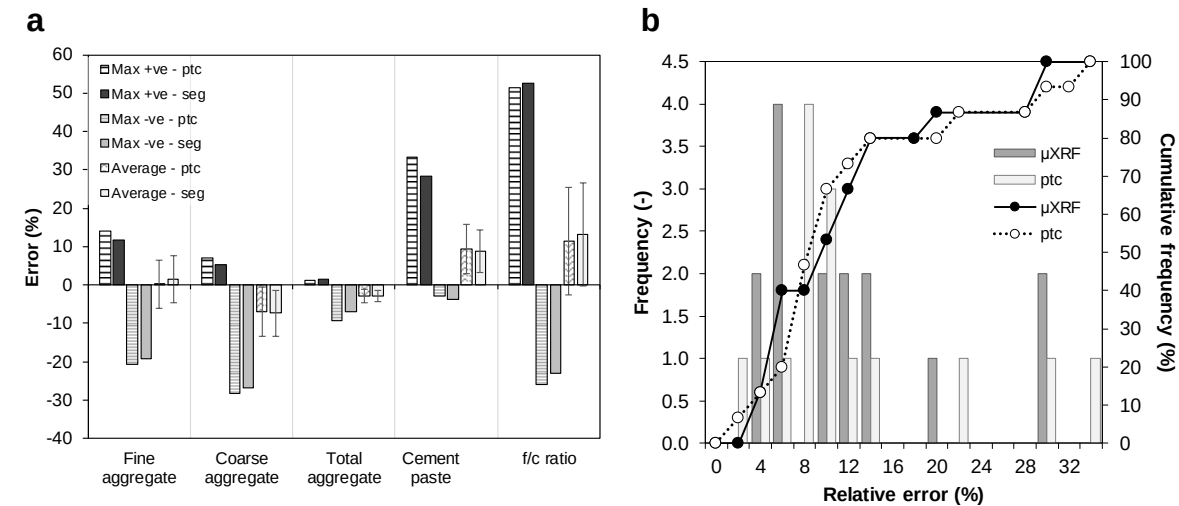
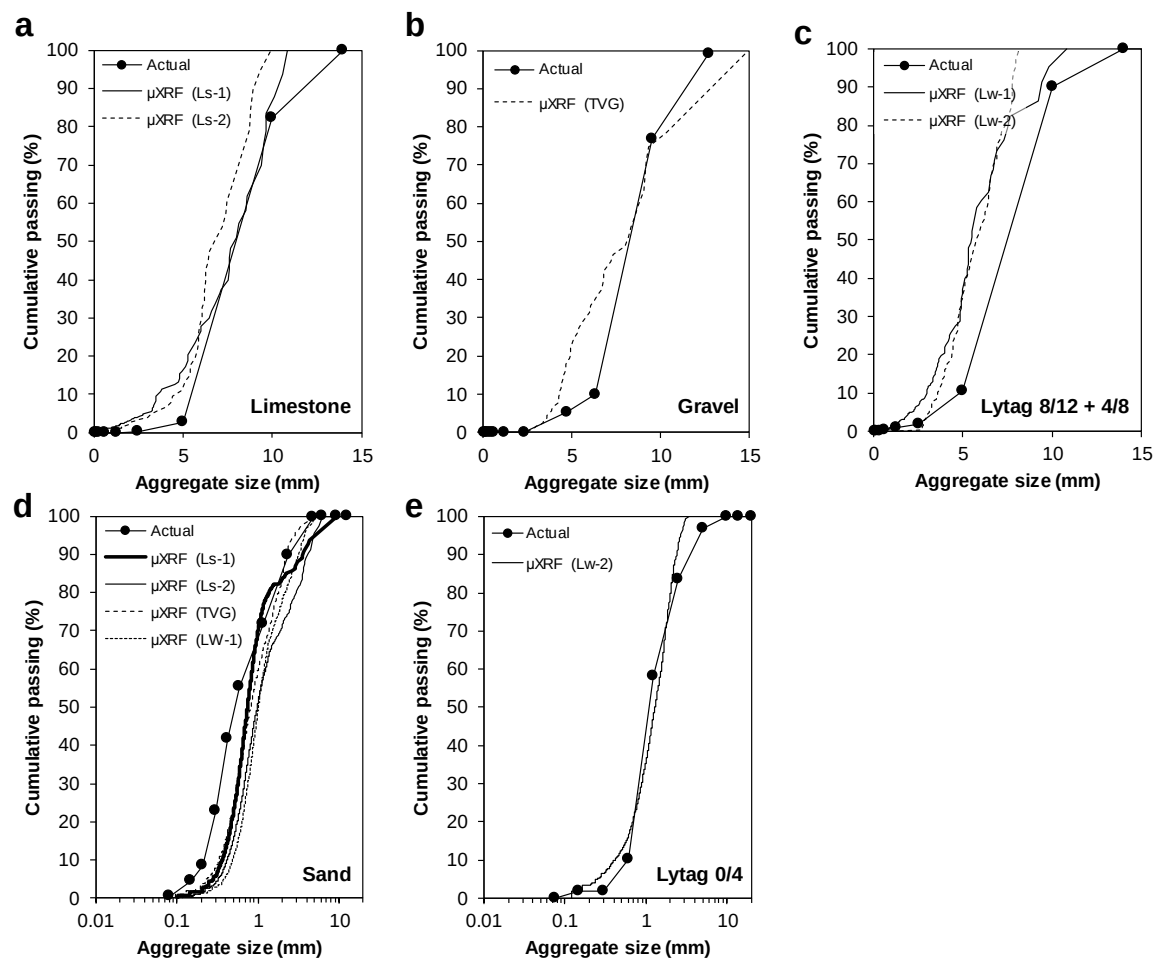


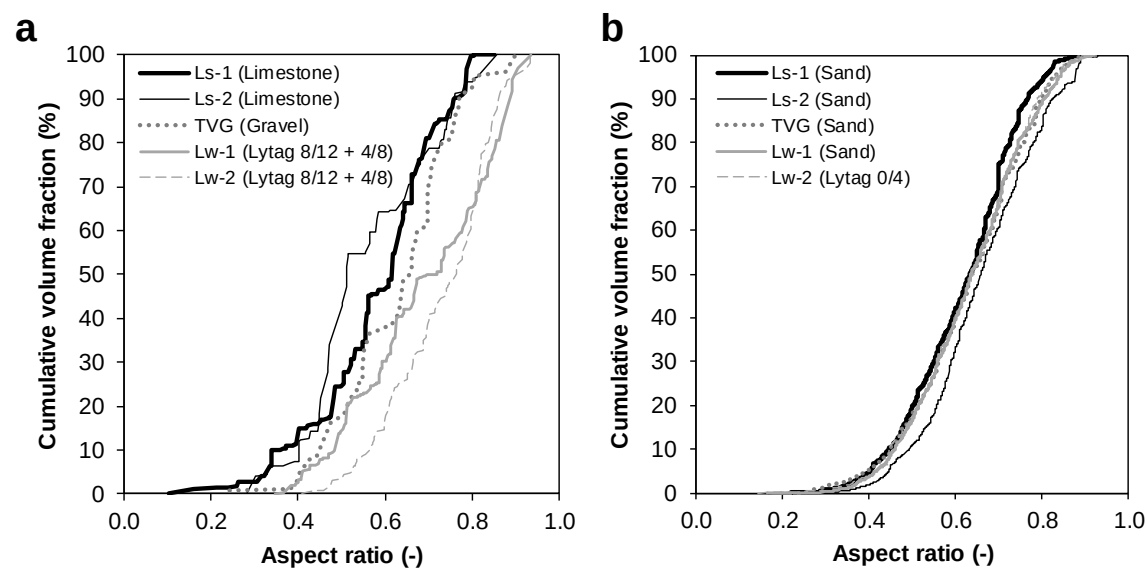
Fig. 7 Maximum +ve and -ve errors, and average errors (a) and frequency and cumulative histograms of absolute error (b) in measured fine and coarse aggregate and cement paste contents. Error bars in (a) represent $\pm$ one standard error.



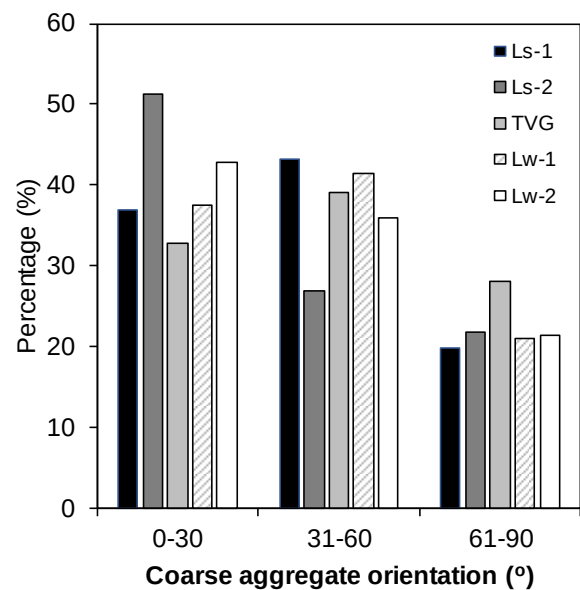
510 **Fig. 8 Comparison of particle size distributions measured with image analysis (μ XRF) and sieve analysis for coarse (a-**
511 **c) and fine (d-f) aggregates.**



514 Fig. 9 Aspect ratio of coarse (a) and fine (b) aggregate particles.

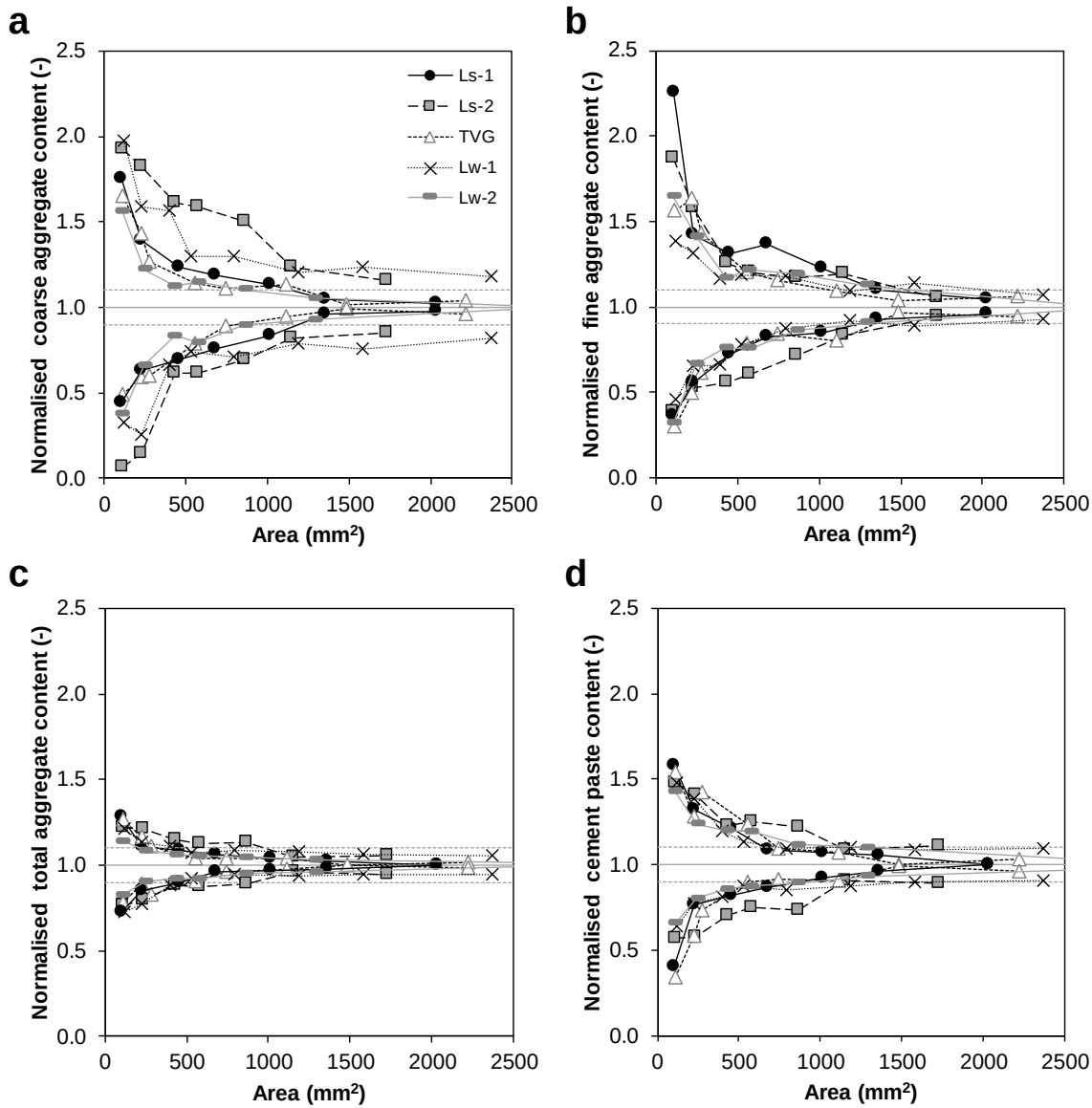


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517 Fig. 10 Orientation of coarse aggregate particles.

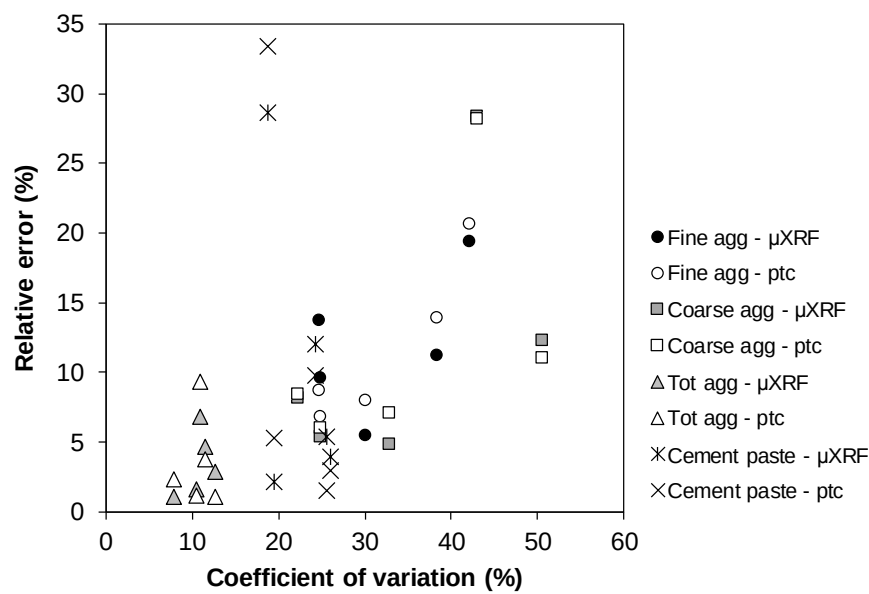


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519 Fig. 11 Effect of image size on the measured contents of coarse aggregate (a), fine aggregate (b), total aggregate (c)
520 and cement paste (d). Horizontal dash lines mark ± 0.1 boundaries.



523 **Fig. 12 Relative errors (%) in the measured fine aggregate, coarse aggregate and cement paste contents vs.**
524 **coefficient of variation of contents measured from subsampled images of ~110 mm².**



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