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Old Dogs and New Tricks: Adapting Existing Analytical E-Beam Equipment for Automated Large-Area Quantitative Elemental Mapping of Chlorine in Cement, Mortar and Concrete

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Cements, mortars and concretes have been used in structures since antiquity and continue to be some of the most commonly used structural materials today [1]. Cementitious materials are famously strong in compression and weak in tension and hence are commonly reinforced with steel rebar [1]. The cementitious phase of mortars and concretes is known to be porous however, enabling the ingress of reactive species [1, 2]. Chlorides are of particular interest in reinforced structures as concentrations in the range of 0.6 to 0.9 kg/m^3 are sufficient to depassivate the steel rebar and initiate corrosion [1]. Oxidation of rebar is accompanied by an increase in its volume that ultimately causes cracking and spalling of the encasing mortar or concrete; these changes greatly enhance the transport of reactive species which can facilitate intense rebar corrosion and potentiate structural failure [1].

Concrete structure is extremely heterogeneous within length scales ranging from microns to centimeters (10^{-6} m – 10^{-2} m) [1]. The cement paste or binder portion of a concrete is specifically highly variable from a microscopic – microanalytical standpoint with the quantities of cement, pores, sand, rock, salts and minerals typically fluctuating from one voxel to the next. Chloride penetration and diffusion into concrete (assumed to occur primarily via the porous cement paste phase of intact concrete [2, 3]) results in an entangled distribution of chlorides within the paste microstructure.

In an effort to both qualitatively and quantitatively characterize this entangled chloride distribution within concrete, Mori et al. have developed an "area analysis" or large-scale elemental mapping technique using electron probe microanalysis (EPMA) [3]. In this method, electrons focused into a beam (microprobe) normal to the sample surface are made to impact a polished, conductively-coated concrete specimen held within a vacuum chamber. This e-beam interrogation generates a quantifiable distribution of x-rays characteristic of the local elemental composition of the sample. X-rays of wavelengths characteristic to specific elements comprising the sample are then collected and measured using wavelength dispersive spectroscopy (WDS). This compositional information coupled with knowledge of the particular spot interrogated on the sample surface (x, y, z) creates a pixel. Moving the sample regular intervals (e.g., 100 μm steps) under the fixed beam enables the collection of large numbers (10^5) of these pixels that can then be combined to construct large-scale compositional X-ray maps with sub-millimeter resolution. The concentration (local and regional) of an element of interest such as chlorine can be quantified from a map via comparison to appropriate reference standards and standard curves [3, 4]. This type of large-scale quantitative X-ray mapping technique has the potential to supplant tradition wet-chemical approaches currently used to develop chloride concentration profiles and calculate diffusivities (D_a) of chlorine in reinforced concrete structures [3, 4]. Therefore, this new method could have widespread and significant impact in the

evaluation of durability [3, 4]. Furthermore, this microanalytical method is non-destructive, does not generate hazardous chemical waste, and is potentially faster and more cost-effective over the long term.

Executing this X-ray mapping technique with a newer (< 5 – 10 yrs. old) EPMA that has all the needed capabilities "from the factory" is relatively straightforward; however, achieving this kind of analysis with existing older e-beam equipment is less so. We describe here our success adapting existing e-beam equipment to perform this quantitative X-ray mapping analysis on concrete. By combining in-house computer programming with the NIH public domain image processing program ImageJ, a standard Cl calibration curve (Fig. 1) and large-scale compositional X-ray maps (Fig. 2) were obtained. This powerful new method of concrete analysis may therefore be more widely used and investigated by maximizing existing analytical instrumentation [5].

References

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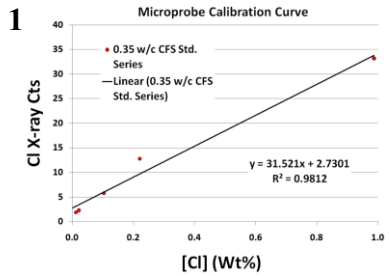

FIG. 1. Calibration curve developed on a JEOL Superprobe 733 linking measured Cl X-ray counts (normalized) with known [Cl] levels in prepared mortar standards.

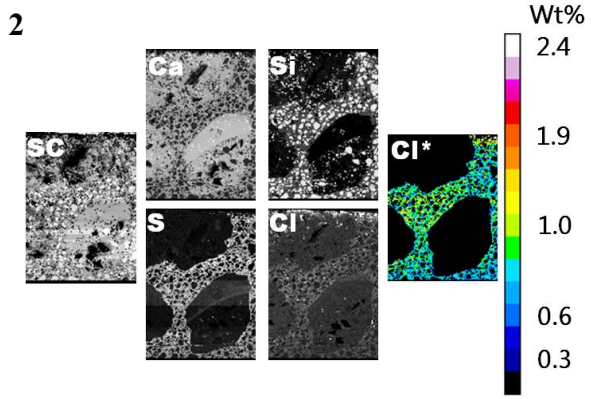

FIG. 2. Specimen current image and corresponding elemental X-ray maps of a concrete sample constructed from data collected with a JEOL Superprobe 733. Wt% scale applies only to Cl*. Image width = 1 cm for all. SC = Specimen Current image, Cl* = Processed paste-only Cl X-ray map.

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