Energy Dispersive X-ray Spectrometry for Determining Chloride Concentration Profiles in Concrete

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Abstract: Assessing the condition or durability performance of existing reinforced concrete infrastructure can involve a broad range of investigation techniques. Investigations during the life of the structure can be used to inform the asset management process. A typical test regime will involve visual inspection, cover meter surveys, electrochemical testing, strength assessments, and the collection of core samples for a range of analytical chemical testing. In cases where there is a perceived risk of Alkali-Silica Reaction occurring, the testing regime may also include uranyl acetate fluorescence screening, or petrography. Petrography can be done using optical microscopy or Scanning Electron Microscopy (SEM). While petrography can be used to determine the likelihood of ASR, it is also able to give an indication of other concrete properties including, porosity, cement content, and strength. SEM petrography with the combination of Energy Dispersive X-Ray Spectroscopy (EDS) can also provide semi quantitative assessment of other properties including but not limited to; aggregate cement ratio, and chloride content. In this paper, we propose that the use of SEM petrography and EDS can provide a more efficient and cost effective way to gather most of the information required to perform durability assessments of existing structures. While the use of SEM petrography is not a new concept, using EDS to determine chloride concentration profiles is a novel approach. In this paper, we compare chloride profiles from SEM-EDS against those gained from conventional wet chemistry. The results from both assessment techniques were fit to estimate the apparent chloride diffusion coefficients.

1.   Introduction

Reinforced concrete is one of the most widely used construction materials in the world. Most of the bridges and major marine infrastructure in Australia consists of reinforced concrete structural elements. Today the importance of concrete durability is widely accepted and incorporated into the design process for most major infrastructure. It is also an important consideration in the monitoring, maintenance and management of existing structures. Major infrastructure owners such as the state roads and port authorities have systematic asset inspection programs to monitor the condition and deterioration of their reinforced concrete structures. These inspection programs often incorporate periodic detailed assessments of the reinforced concrete elements to determine the risk of corrosion activity. These assessments are typically referred to as Level 3 inspections within the road authorities. In the ports sector the current best practice for these types of assessments is outlined in the Wharf Structures Condition Assessment Manual [1] published by Ports Australia.

The Inspection guidelines published by the road authorities [2,3 and 4] and Ports Australia [1] include procedures for a range of investigation techniques including but not limited to; visual, delamination, cover meter, rebound hammer, half-cell potential, corrosion rate, resistivity, cement content, chloride profile, depth of carbonation and petrography. The inspector typically uses a combination of these techniques to develop an understanding of the structures current condition, the cause of deterioration, and the risk of future deterioration. Testing properties like strength, cement content, carbonation, and chloride profiles require the extraction of core samples from the concrete. These samples are then sent to analytical laboratories for testing.

The standard practice for determining chloride concentration profiles in concrete is to section the core samples into discrete depth increments, typically around 10-25mm thick. While it is possible to do much thinner sections (2-5mm) this is typically not done due to cost constraints. The sectioned samples are then crushed, digested in acid, and the chloride concentration determined by end point titration. This gives the approximate average chloride concentration within the concrete segment as a wt.% concrete (or cement if the cement content is known). The methodologies typically used in Australia are detailed in BS 1881-124:2015 Testing concrete. Methods for analysis of hardened concrete, and AS 1012.20-1992 Methods of

testing concrete Method 20: Determination of chloride and sulfate in hardened concrete and concrete aggregates.

The results from the chloride concentration testing is then used to prepared chloride concentration depth profiles. The profiles are used to determine the risk of corrosion at the time of testing, as well as into the future. The diffusion coefficient D_t of chlorides in concrete is typically estimated by fitting the chloride concentration depth profiles with Cranks' solution to Fick's second law of diffusion Equation 1 [5]. However, more sophisticated methods have been proposed by some authors [6,7 and 8].

$$C_{(x,t)} = C_s \left(1.erf \left(\frac{x/2}{\sqrt{D_t}} \right) \right)$$ (1)

The prediction of time to corrosion initiation and subsequent cracking or delamination of the concrete is a complex process and the outcomes of modelling is subject to a broad range of variables. Finite and probabilistic prediction models are both used in practice today [9]. A finite model will produce a specific time to corrosion initiation and cracking based on the input variables. While probabilistic models return a characteristic time, frames based on a range of input variables.

Producing chloride profiles using the currently accepted titration methods presents some limitations:

1. The process is destructive and the sample is destroyed in the analysis process. Because of this it is not possible to perform any other tests on the same sample. Furthermore, to produce duplicate or triplicate results to determine variability requires multiple samples or sub samples.
2. The resolution of the test is limited due to the process of sample preparation. Sectioning samples into 10-25mm sections only makes it practical to typically determine 3-4 points within the cover zone. Furthermore, for relatively young structures the chloride uptake may only be significant within the first 10-15mm of the cover concrete.
3. The process of sample preparation, digestion and analysis typically takes a minimum of 3 days. However, in practice it can take weeks to process large batches of samples.

It is proposed that using Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS) to produce total chlorine concentration profiles for concrete samples presents a suitable alternative to the current wet laboratory practices. The benefits for SEM and EDS include:

1. SEM-EDS analysis can be used to produce high resolution elemental concentration maps that can be used to quantify the concentration of total chlorine relative to the cement content.
2. Multiple chlorine profiles can be determined from different locations on a single sample.
3. Other elements can also be investigated including Ca, Si, and S.
4. The same sample can be used to for SEM petrography to determine a range of properties and features including but not limited to; cement content, porosity, microcracking, alkali-silica reaction, delay ettringite formation, aggregate cement ratio, water cement ratio, and aggregate characterization.

It is also considered viable that X-ray fluorescence (XRF) could be used for the determination of concentration profiles. Mehdi, et. al. have demonstrated the use of X-ray imaging techniques to investigate the ion diffusion in cementitious laboratory samples [10,11 and 12]. Using microXRF the Author demonstrated a good correlation between results from titration and microXRF. Ultimately, it would be ideal to be able to use hand held XRF devices in the field to provide initial chloride content assessments. This will be the subject of future studies.

This initial paper presents the chlorine concentration profiles taken from 2 samples using SEM-EDS and compares them against chloride concentration profiles derived by titration of 2 samples taken from the same structures.

2. Methodology
2.1 Test Samples

Tests samples were collected from two existing bridge structures in Australia:

- Bridge A, was constructed in 1959 and crosses an estuary
- Bridge B, constructed in 1977 and adjacent to an estuary

The test samples were 50mm diameter cores secured by wet diamond core drilling.

2.2 Titration Chloride Content Analysis

One core sample from each bridge was sent for chloride content analysis by end point titration. The samples were sectioned into 4 segments and crushed for analysis. The depth range for each segment is shown in Table 1 below.

Table 1. Sample details for titration chloride content analysis

Sample ID	Bridge	Segment depth range (mm)	Segment depth range (mm)	Segment depth range (mm)	Segment depth range (mm)
1	A	0-15	15-30	30-45	45-60
2	B	0-15	15-30	30-45	45-60

The chloride content of each segment was determined in accordance with BS 1881. The results were presented as wt.% concrete and plotted against depth. The reported chloride concentration was the average across each segment and the depth was taken as the mid-point.

2.3 SEM EDS Chloride Content Analysis

One core sample from each bridge was prepared for SEM-EDS analysis. The sample IDs were as follows:

- Sample 1-EDS was from Bridge A
- Sample 2-EDS was from Bridge B

Each core sample was sectioned longitudinally and dry polished by hand using a 60 grit belt sander followed by 120 grit, 240 grit, 400 grit, 600 grit, 800 grit then 1200 grit paper. The dry polishing was used to avoid movement or dissolution of chloride in the sample. The cores were carbon coated prior to analysis. Non-conducting samples require coating prior to SEM analysis to prevent charging by the incident electron beam.

The sample was analysed using a Carl Zeiss EVO50 HD15 SEM fitted with an Oxford INCA X-Max energy dispersive X-ray spectrometer (EDS). Elemental (X-ray) maps were taken at 23x magnification to give 5mm fields. Each elemental map was taken for 8 frames at 512x384 pixels.

The elemental concentrations were normalised without carbon to account for the carbon coating, and the approximate carbon content was calculated from the calcium concentration using the assumption that all calcium was present as calcium carbonate. The chlorine concentration was adjusted accordingly.

The chlorine concentration was reported as the wt.% of the total sample across 5mm segments and averaged across 15mm segments to match those from the titration analysis.

2.3 Chloride Diffusion and Time to Corrosion Modelling

The chloride content results were plotted in excel and curve fitting was used to estimate the apparent diffusion rate of chlorides (m^2/s) and the surface chloride content (wt. % concrete) given by Crank's solution to Fick's second law of diffusion, which has the form given in Equation 1.

Where:

- $c(x,t)$ is the chloride ion content at depth x and time t, in wt. % cement.
- c_i is the initial chloride ion content cast into the concrete, also called background chlorides, in wt. % concrete
- c_s is the apparent surface chloride ion content, in wt. % cement.
- erf is the error function.
- D is the apparent diffusion rate of chloride ions, in m2/s

3. Results and Discussion

The results from the titration chloride content analysis are presented in Table 2. Both samples show concentration profiles typical of concrete exposed to an environment where external chloride contamination occurs, with a high concentration at the surface that tapers off with depth. Sample 1 shows a slightly higher chloride content within the first increment, while the concentrations at depth are within the typical margin of error for this measurement technique.

Table 2. Titration chloride content analysis results

Sample ID	Bridge	Chloride wt.% Concrete			
		0-15 (mm)	15-30	30-45	45-60
1	A	0.11	0.04	0.03	0.02
2	B	0.05	0.03	0.01	

Figure 1 a) and b) show SEM images of the sample field where the EDS composition mapping was performed over the first 0-15mm depth increment. The actual fields were 3.8mm in the y direction and a total of 60mm in the x direction for sample 1-EDS, and 40mm for sample 2-EDS.

a)

b)
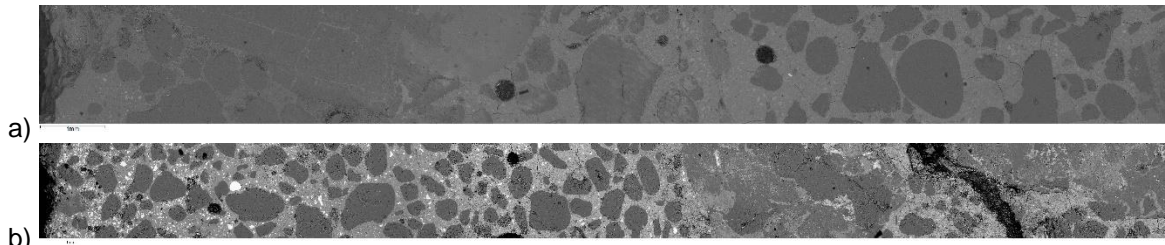
Figure 1. SEM images of the sample field where the EDS composition mapping was performed over the first 15mm of the samples a) Sample 1-EDS Bridge A b) Sample 2-EDS Bridge B

Table 2 shows the chloride concentrations determined using EDS as a wt.% of the total sample. These results were adjusted to account for the carbon coating. The concentrations from the EDS were determined for every 5mm increment taken along the sample area. The results for sample 1-EDS shows a significantly higher chloride content within the first 2 increments as compared to those at depth. The results for sample 2-EDS are more inconsistent across the sample. Initially they show a typical profile, however, at depth they are more stochastic before tapering off to zero. It is important to note that it is very unlikely that there is no chlorine present. This result suggests that the technique may lack the required resolution at low concentrations.

Table 3. Sample details for titration chloride content analysis

Sample ID	Bridge	Chloride wt.% Concrete											
		0-5	5-10	10-15	15-20	20-25	25-30	30-35	35-40	40-45	45-50	50-55	55-60
1-EDS	A	0.15	0.13	0.09	0.02	0.06	0.05	0.08	0.00	0.00	0.04	0.04	0.00
2-EDS	B	0.05	0.04	0.02	0.00	0.08	0.05	0.00	0.00				

Visually, the elemental chlorine maps from the samples show a concentration gradient. This gradient was most prevalent for the chlorine map within the 0-5mm region from sample 1-EDS. The dark areas in the chlorine map on the right coincide with the aggregate, which is to be expected as they will not contain chlorine. There is also an apparent band of lower chlorine concentration within the first 1mm of the map, and then a higher concentration band within the next 1mm band. The apparent concentration then gradually tapers off with depth. This is a phenomenon known as the surface convection zone, as reported by Ann et al. [13].
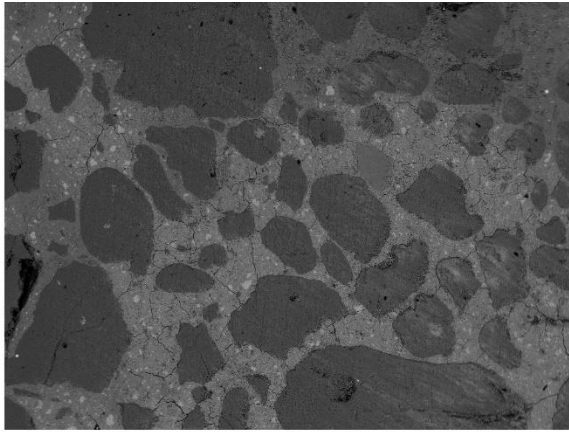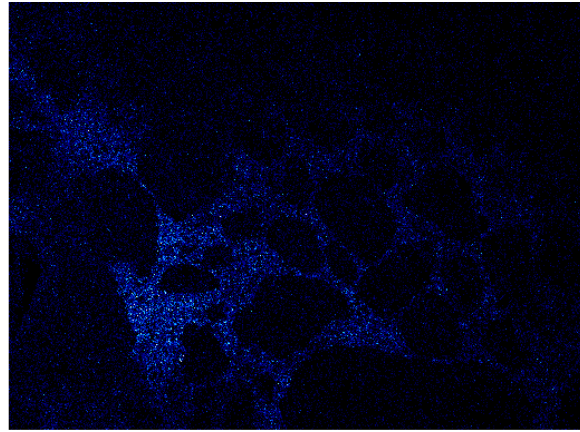
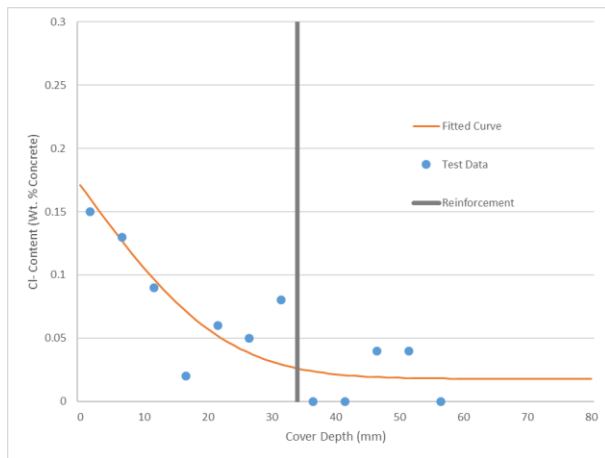**Figure 2. SEM image of 0-5mm region for Sample 1-EDS (left) and Chlorine map for same region (right)**

To compare the data from the titration tests and SEM-EDS, average chlorine concentrations were taken across the equivalent regions from the EDS results and presented in Table 3 Below. For the samples from Bridge A there was good agreement between the results from the two methods. All the concentrations calculated from the EDS results were within 0.01 wt.% of the results from the titration, which is within the typical margin for error. Most of the results for Bridge B were also within the same margin of error; apart from the results for 15-30mm, which were 0.2 wt.% greater than the result from the titration within the same region.

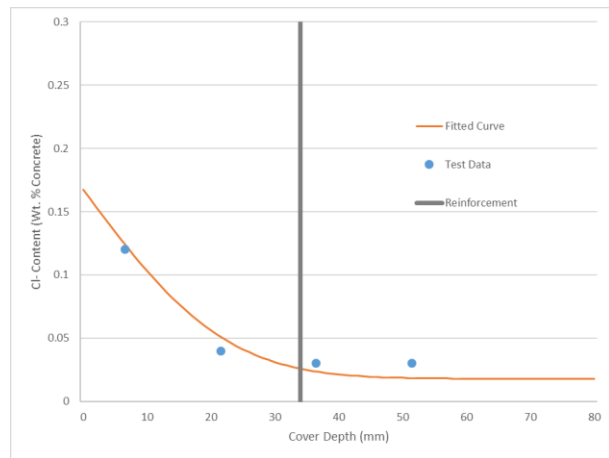**Table 4. Sample details for titration chloride content analysis**

Sample ID	Bridge	Chloride wt.% Concrete			
		0-15 (mm)	15-30	30-45	45-60
1	A	0.11	0.04	0.03	0.02
1-EDS	A	0.12	0.05	0.03	0.03
2	B	0.05	0.03	0.01	
2-EDS	B	0.04	0.05	0.00	

The chlorine profile data from the SEM-EDS investigations was plotted against depth. The diffusion coefficient D_t of chlorides in concrete was then estimated by determining curves of best fit using Cranks' solution to Fick's second law of diffusion (Equation 1). Figure 3 shows the curve fits for the EDS data. Both the full data sets and the average data sets were fit for comparison against the results from fitting the titration data. The curves for the full datasets show that there is a large data spread for concentrations below 0.1 wt.% Cl. However, the fit to the data averages was much closer.

The estimated chloride diffusion coefficients from the EDS and titration data sets are provided in Table 5. The results from Bridge A show good agreement between the data fits from titration samples and the SEM-EDS. However, the results from the fit to EDS data was significantly different to that obtained for the titration data. This is owing to the poor fit of the data within the lower concentration range, and the apparent background chloride content of zero. As discussed previously it is very ulikley that there is an actual chloride content of zero.
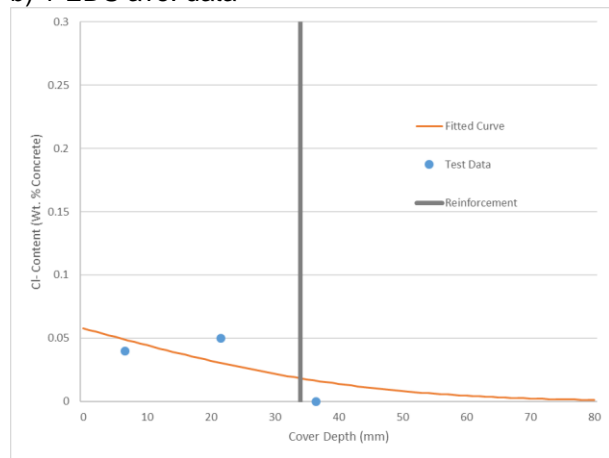
a) 1-EDS all data

b) 1-EDS ave. data
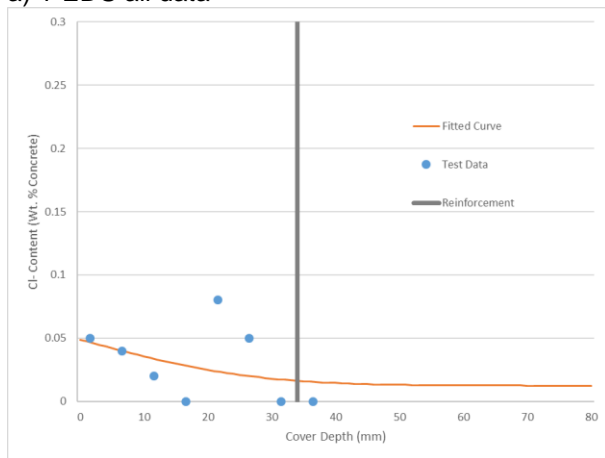
c) 2-EDS all data

d) 2-EDS ave. data

Figure 3. SEM image of 0-5mm region for Sample 1-EDS (left) and Chlorine map for same region (right)

Table 5. Sample details for titration chloride content analysis

Sample ID	Surface Chlorides Conc. (wt.% Concrete)	Background Chlorides Conc. (wt.% Concrete)	Chloride Diff. Coef. (x 10^{-12} m²/s)
1	0.15	0.02	0.09
1-EDS all data	0.17	0.02	0.10
1-EDS ave. data	0.17	0.02	0.10
2	0.07	0.01	0.18
2-EDS all data	0.05	0.00	0.54
2-EDS ave. data	0.06	0.00	0.47

4.   Conclusions

The data presented herein, demonstrates that SEM-EDS shows promise as an alternative technique for accurately determining chloride concentration profiles in concrete. However, there is need for further testing and refinement of the methodology required before it could be realistically considered as a replacement for traditional end-point titration methods.

The primary benefits of using SEM-EDS is that high resolution data is easy to achieve in a relatively short time frame from a single sample. The sample can also be used to determine a range of other concrete properties through SEM petrography.

The authors are currently working on preparing standard samples to directly determine the accuracy of the technique and further refine the process. This will be coupled with wider testing of field samples for comparison.

5. Acknowledgement

6. References

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