Analysis of Efflorescence Contents to Diagnose Concrete Degradation

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1. Introduction

A well-built reinforced concrete structure can last for decades, and even centuries, with proper maintenance. Rebar corrosion is the leading cause of concrete degradation. Some of the factors that can induce rebar corrosion and reduce the life of a concrete structure include: varying humidity, rain and snow, freeze and thaw cycles, and especially calcium chloride from ocean spray or from de-icing salt treatments. Early detection of potential problems could reduce repair and replacement costs. The goal of this research is to determine whether the early signs of rebar corrosion can be diagnosed easily by examining efflorescence, a white calcium carbonate material that sometimes exudes from concrete.

Concrete is a combination of siliceous sand, larger aggregate rock, and cement, which is a paste of calcium silicate hydrates polymerized into a densely cross-linked matrix[1]. Cement powder is mixed with water to form cement, and a series of reactions takes place over the course of weeks. Finally, it hardens into a suspension of calcium hydroxide, unreacted materials in a solid calcium silicate hydrate (CSH) gel[1], and ettringite, a mineral containing calcium oxide, aluminum oxide, and calcium sulfate. Hardened cured concrete has tiny capillary pores throughout the solid CSH gel and larger void spaces around the aggregate. Concrete is reinforced with steel bars (rebar) to improve its tensile strength. Rebar is protected from corrosion by the high pH of concrete, which allows the formation of a thin passive oxide layer on the surface of the metal.

Reinforced concrete is often degraded by the action of water[1]. When water filling the concrete pores and voids freezes, its increased volume exerts pressure on the pore walls causing microcracking. Repeated freeze and thaw cycles extend the cracks until they are visible macroscopically. This allows penetration of water further into the structure. Water penetration can lead to carbonation, the formation of calcium carbonate, which occurs when carbon dioxide diffuses into the concrete and dissolves in the water within the pores. Calcium hydroxide near the pores in the cement matrix reacts with the dissolved carbon dioxide and forms calcium carbonate. When carbonation forms near the surface of the concrete, it can ooze from the pores, leaving a white material on concrete walls or stalactites on concrete ceilings. This efflorescence can be an external sign of water seepage problems within the structure[1].

As calcium hydroxide leaches out of the concrete, chloride ions can also leach in. Sodium chloride from ocean spray or de-icing salts provide these chloride ions, which can be transported by capillary suction or by differences in pressure gradient, concentration gradient, and electric potential[5]. When calcium hydroxide leaches out, and chloride ions are transported in, together they lower the concrete pH below a threshold level. This lower pH can cause the protective oxide layer around the rebar to dissolve, called depassivation, which allows extensive rebar corrosion.

Steel rebar is 97-98% iron, 1.1% manganese, 0.37% copper, 0.11% nickel, and other trace elements[6]. When the metals form oxides, they have a much greater volume than the original steel. This causes stress on the surrounding concrete, resulting in cracking; spalling, when chunks of concrete break off; and delamination, when concrete separates from the rebar[5]. This irreparable damage may be avoided if problems from carbonation can be detected early enough and remedied. Papadakis and Fardis showed that a 20 mm lime-cement mortar coating can arrest the advancement of carbonation and reinstate alkalinity (raise pH) to above the threshold level of steel depassivation[4].

This research is a preliminary study to investigate if the internal state of reinforced concrete can be determined by examining efflorescence from concrete. Stalactites from 10, 40, and 110 year old reinforced concrete structures were analyzed. The inductively coupled plasma mass spectrometer (ICP-MS) was used to measure iron, manganese, copper, and nickel content to determine if early products of rebar corrosion are present in the efflorescence. The results of the investigation may help uncover a simpler, more cost effective method of determining whether examining efflorescence could be used as a diagnostic tool.

2. Theory

The counts per second (CPS) output from the ICP-MS was analyzed using a variation of the Beer-Lambert law. Scandium was chosen as the internal standard because it is unlikely to be in the sample, and it is within 20 mass to charge ratio from the elements of interest. The internal standard was used to account for variance in sample introduction. The ratio of CPS analyte over CPS internal standard in the blank was subtracted from the same ratio in the standards. The result, called the net intensity mean (NIM), was used to plot the standard curves, which were used to determine the concentration of metals in solution. See an example in figure 1. An R^2 value of 0.9998 or better is desired.

$$\frac{\text{CPS analyte in standard}}{\text{CPS internal std in standard}} - \frac{\text{CPS analyte in blank}}{\text{CPS internal std in blank}} = \text{NIM}$$

Figure 1. Iron Standard Curve.

3. Experimental

3.1 Sample Collection

Calcium carbonate efflorescence stalactites were gathered from three different locations. The oldest concrete sampled was from Fort Canby, Battery Harvey Allen, built in 1905. The other two samples were collected from Evergreen State College, one from the College Recreation Center (CRC), built in 1972, and the other from the Seminar II building, built in 2002. Care was taken to avoid contamination using latex gloves and plastic instruments for sample collection. Any contact with metals was carefully avoided. Samples were collected in December and April; months of heavy rainfall. Samples were stored in Ziploc® bags.

All glassware and materials used in this experiment were washed, soaked in a nitric acid bath for at least 12 hours, and triple rinsed with deionized water. The mortar and pestle was acid washed and allowed to dry for several hours before grinding each sample to a fine powder.

The sample from Fort Canby (location 1) was brownish and varied in color, the one from the CRC building (location 2) was tan colored and fairly uniform , and the one from the Seminar II building (location 3) was uniformly bright white colored. The powdered samples were stored in small polypropylene bottles.

3.2 Digestion

The solutions used for digestion were Mallinckrodt® 30% H_2O_2, concentrated and 1:1 HNO_3 prepared from concentrated OmniTrace® metals grade nitric acid.

A modified version of EPA method 3050B[7] for acid digestion was used. The powdered material from each location was used to prepare three samples (A, B, and C) for iron detection and two additional samples (D and E) for copper, manganese, and nickel detection. Each 100.0 mg sample was weighed on an analytical balance, in 100 mL beakers. Ten mL of 1:1 HNO_3

was added to each sample beaker and method blank beaker. After adding acid, samples from locations 1 and 2 were yellowish in color, with sample 2 more intense yellow. The sample from location 3 was colorless.

Each beaker was placed on a hot plate, covered with a watch glass, and heated to 70°C for 15 minutes. These were then cooled, and 5 mL concentrated HNO_3 was added. The samples were heated again, to 80°C for 10 minutes. No brown fumes were generated, indicating that this step did not need to be repeated. Heating continued for two hours to evaporate the contents. All beakers were then cooled and 2 mL deionized water and 3 mL H_2O_2 were added. The beakers were returned to hot plates and some effervescence was noted upon heating. At this point, the samples were colorless and completely digested. Evaporation was repeated, and most samples evaporated to 5-10 mL within 90 minutes.

Contents were quantitatively transferred to 100 mL volumetric flasks by gravimetric filtration with Whatman® filter paper. Each sample was stored in a small polypropylene bottle and refrigerated.

3.3 Sample Dilution

For iron detection, 2 g of internal standard solution and 1 g of 1:1 HNO_3 was added to 2 g of each sample solution and diluted to a total of 10 g. In addition, for each sample "C", another dilution was prepared and spiked with 200.0 mg of iron intermediate solution to test for iron recovery. See results in Tables 2 and 3.

For copper, manganese, and nickel detection, 2 g internal standard solution and 1 g 1:1 HNO_3 was added to 7 g of each sample solution.

3.4 Standards Preparation

The internal standard solution was prepared with a stock scandium solution and deionized water.

For intermediate standard solutions, each copper, iron, manganese, and copper stock solution was combined with deionized water and 1:1 HNO_3 to stabilize.

The high, medium, and low standards were prepared from intermediate standard solutions, 2 g internal standard solution, 1 g 1:1 HNO_3 to stabilize, and deionized water to a total of 10 g. See Table 1 for concentrations.

The matrix blank was prepared with 2 g internal standard solution, 1 g 1:1 HNO_3, and deionized water to a total of 10 g.

Table 1.

Standards Preparation, Dilutions, and Concentrations.

	Internal standard	**Iron**	**Nickel**	**Copper**	**Manganese**

Initial stock concentration	1000 ppm	1000 ppm	1000 ppm	1000 ppm	1000 ppm
First dilution	1:25	1:100	1:100	1:100	1:100
Additional dilution	1:100	_	1:100	1:100	1:100
Intermediate concentration	400 ppb	10 ppm	100 ppb	100 ppb	100 ppb
High standard	80 ppb	500 ppb	10 ppb	1 ppb	1 ppb
Med standard	80 ppb	250 ppb	5 ppb	0.50 ppb	0.50 ppb
Low standard	80 ppb	50 ppb	1 ppb	0.25 ppb	0.25 ppb

4. Instrument

The Perkin Elmer DRC-e Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used in this experiment. The instrument has detection limits as low as one part per trillion under optimum conditions, but provides best results at 1-10 parts per billion (ppb), for the elements analyzed in this work. All analytes of interest can be analyzed at once in the ICP-MS.

Samples must be in a dilute liquid solution for injection into the instrument. They must contain less than 0.2% total dissolved solids by weight in a matrix of one percent nitric acid.

A daily performance check is used to ensure that the instrument is running optimally. Data output is analyzed for consistent sample introduction, and detection at the correct concentration of various ions in a test solution.

5. Results and Analysis

The results from iron detection show that the amount of iron in the efflorescence from each location was precise, with a relative standard deviation of 5.36 percent. The results after subtracting the iron spikes from samples “C1” were consistent with other samples, showing that the method did not introduce or remove iron from the samples. See Tables 2 and 3.

The results from nickel detection were also precise, with a relative standard deviation of 3.66 percent. The results from copper and manganese detection show greater variation. See Table 4.

Table 2.

Analysis of Iron in the Samples from Locations 1 and 2.

	1A	**1B**	**1C1**	**1C2**	**2A**	**2B**	**2C1**	**2C2**
Sample prep								
Mass of sample (g) in 100 mL	0.0998	0.1095	0.1083	0.1083	0.1028	0.1009	0.1021	0.1021
Mass of solution (g)	2.0001	2.0146	1.9969	2.0082	2.0053	2.0192	1.9919	2.0138
total solution (g)	10.000	10.016	10.000	10.012	10.014	10.013	10.009	10.031
Concentration of original sample (ppm)	199.6	220.2	216.3	217.2	205.9	203.5	203.2	205.0
ICP-MS output								
Conc. of Fe in solution (ppb)	287.2	293.2	504.0	287.5	286.5	265.5	466.1	305.5
Fe spike (ppb)			215.0				197.0	
Net Fe in solution - spike (ppb)	287.2	293.2	289.1	287.5	286.5	265.5	269.1	305.5
Net conc. of Fe in sample (ppm)	1439	1331	1337	1323	1392	1305	1324	1490
	Location 1				**Location 2**			
Average Fe in solution (ppb)	1358				1378			
Standard deviation	54.64				83.64			
Relative standard deviation	0.0402				0.0607			

Table 3.

Analysis of Iron in the Samples from Location 3.

	3A	**3B**	**3C1**	**3C2**
Sample prep				
Mass of sample (g) in 100 mL	0.1019	0.1089	0.1091	0.1091
Mass of solution (g)	2.0124	2.0050	2.0069	2.0109
total solution (g)	9.9951	10.010	10.018	10.016
Concentration of original sample (ppm)	205.2	218.1	218.6	219.0
ICP-MS output				
Conc. of Fe in solution (ppb)	271.5	316.3	470.2	291.3
Fe spike (ppb)			201.2	
Net Fe in solution - spike (ppb)	271.5	316.3	269.0	291.3
Net conc. of Fe in sample (ppm)	1323	1450	1231	1330
	Location 3			**Overall**
Average Fe in solution (ppb)	1334			1356
Standard deviation	89.82			72.66
Relative standard deviation	0.0673			0.0536

Table 4.

Copper, Manganese, and Nickel Analysis.

	1D	1E	2D	2E	3D	3E	Overall
Sample prep							
Mass of sample (g) in 100 mL	0.1291	0.1328	0.1302	0.1254	0.1351	.01289	
Mass of solution (g)	7.0225	6.9899	7.0012	7.0228	7.0098	6.9899	
Total solution (g)	10.028	10.022	10.094	10.056	10.009	10.188	
Concentration of original sample (ppm)	904.1	926.3	903.1	875.7	946.2	884.4	
ICP-MS output							
Ni ppb in solution	8.395	8.409	8.750	8.638	9.261	8.817	
Ni ppm in sample	9.286	9.078	9.689	9.864	9.788	9.970	
Average		9.182		9.776		9.879	9.612
Standard deviation		0.146		0.123		0.129	0.352
Relative standard deviation		0.0159		0.126		0.131	0.0366
Cu ppb in solution	6.418	3.748	4.058	3.041	5.725	3.212	
Cu ppm in sample	7.099	4.046	4.494	3.473	6.051	3.632	
Average		5.573		3.983		4.841	4.799
Standard deviation		2.158		0.722		1.710	1.459
Relative standard deviation		0.387		0.181		0.353	0.304
Mn ppb in solution	0.294	0.271	2.279	0.833	0.033	0.079	
Mn ppm in sample	1.473	1.230	11.071	4.094	0.161	0.362	
Average		1.352		7.582		0.262	3.065
Standard deviation		0.171		4.933		0.142	4.166
Relative standard deviation		0.1265		0.6506		0.5420	1.359

6. Discussion

From literature values of rebar content, it was expected that the ratios of manganese, copper, and nickel relative to iron detected would be approximately 1 percent, 0.4 percent and 0.1 percent. The actual ratio of copper to iron detected in the efflorescence is consistent with expectations. However the nickel content is higher than expected, and the manganese content is lower than expected. These differences could be due to varying rates of transition through the concrete, or possible reactions with other components of the concrete.

There was some difficulty achieving consistent results with standards and samples of low concentrations. Although the ICP-MS can optimally detect concentrations in the low parts per trillion, it appears to only be accurate to about 10 ppb under the operating conditions in this lab (not a clean room). In samples with lower concentrations, results varied and standard deviations were high. Similarly, the analytical balance only appears to be accurate to about 10 mg, although all powdered samples and solutions were weighed to 0.1 mg.

Although metals from rebar degradation can be detected in the efflorescence, they do not appear to be a good indicator of the interior state of the concrete. From the cross-section of time and few samples that were analyzed in this experiment, rebar appears to break down and metals appear to leach through concrete at a steady rate. This begins as early as ten years after construction, and continues throughout the life of the concrete.

Future work would include analyzing many more samples, including samples of newer concrete, different types of concrete, concrete without steel reinforcement, and possibly analyzing samples of the concrete itself in addition to the efflorescence. This could help add to the understanding of mechanisms of rebar degradation and metal leaching.

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