### SP-336: Cracking and Durability in Sustainable Concretes

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### INTRODUCTION

Concrete provides a passive corrosion protection for the embedded steel rebars on account of the high-alkaline environment [1]. However, improper design, an aggressive service environment and other facts may accelerate the ingress of chloride ions or other corrosion-causing substance and thus lead to the corrosion of reinforcement steel [2], [3]. Chloride ions from marine environment, deicers and other sources may lead to severe corrosion on reinforced concrete (RC) bridges and RC pavements [4]. After corrosion has been initiated, the volume expansion of corrosion products may induce cracks, and thus reduce the service life and load capacity of the reinforced concrete. Furthermore, these cracks will increase the diffusion of chloride ions into the concrete. As a result, corrosion may propagate even faster [5]. On the other hand, corrosion also can result in loss of the steel reinforcement cross sectional area, which in turn reduce the load capacity of RC structures. Therefore, premature failure of RC structures may occur due to these facts.

The addition of a corrosion inhibiting admixture is a preferred method to prevent chloride-induced rebar corrosion in RC structures [6]. It has the advantages including easy application, cost effectiveness and less side effects compared to other traditional corrosion prevention and protection methods. For instance, the epoxy coatings for rebar are prone to aging, damage and degradation; the use of stainless steel or galvanized reinforcement in concrete results in substantial environmental footprints such as air pollution during their production period [7].

One challenge is that many corrosion inhibitors are toxic and thus may induce harmful health effects and cause environmental concerns [8],[9],[10]. For example, some corrosion inhibiting admixtures will cause temporal or

permanent damage to human organs like kidney and liver [11]. Efforts have been made to use green corrosion inhibiting admixtures, such as inhibitors extracted from plants, to mitigate this problem.

Recent studies on green corrosion inhibitors have shown that they are highly effective and environmentally friendly compared to organic and inorganic inhibitors. Nazari et al. [12] developed a green corrosion inhibitor from waste peony leaves which has a good inhibition effect to protect carbon steel from NaCl. Raja et al. [9] reviewed recent studies of natural corrosion inhibitors, including opuntia ficus indica, arghel extract, bambusa arundinacea, rhizophora mangle and vernonia amygdalina. Besides the inhibitors extracted from natural plants, other green corrosion inhibiting admixtures were also studied. For instance, an eco-friendly biopolymer corrosion inhibiting admixture was investigated and proved to be effective [13],[14].

Based on the successful development of peony-leave based corrosion inhibitors [12], this study further investigated four types of liquid admixtures as green corrosion inhibitors, which were extracted from peony leave, Kentucky blue grass, sugar beet leave and dandelion, respectively. The influence of these four green admixtures on mortar properties were evaluated. Test methods including 7, 14, 28, and 56 days compressive strength test, rheology test, setting time test, water absorption test, gas permeability test and rapid chloride migration (RCM) test were employed. Furthermore, the inhibiting efficiency of the corrosion inhibitors were measured using electrochemical methods (open circuit potential (OCP) [15], electrochemical impedance spectroscopy (EIS) [16] and linear polarization resistance (LPR) [17]).

### **EXPERIMENTAL**

#### Materials

An ASTM C150-07 [18] Type I/II low-alkali Portland cement was used in this study. Siliceous sand, complying with ASTM C144 [19], was used as fine aggregates. Steel rebar in 3/8 in. (9.5 mm) diameter, complying with ASTM A1035 [20], was used as concrete reinforcement. Four types of liquid corrosion inhibitors were extracted from peony leave (PL), Kentucky blue grass (KG), sugar beet leave (SL) and dandelion (D), respectively, through a zero-waste chemical/biological process [12].

#### **Sample Preparation**

Table 1 listed the material proportion of four groups of mortar mixed with green corrosion inhibiting admixtures and a control group. The cement and sand were mixed first in a concrete mixer for 1.5 minutes. Then green admixtures were added into water before mixing with the cement and sand for another 1.5 minutes. The fresh mixture was cast into 2 in. ×4 in. (5cm ×10cm) cylindrical molds for reinforced mortar specimens and 4 in. ×8 in. (10cm ×20cm) cylindrical molds for Rapid Chloride Migration (RCM) test specimens. All the specimens were demolded after curing at room temperature for 24 hours. They were then cured in a moisture container at 23°C with relative humidity of over 95% for 27 additional days. Mortar samples for corrosion monitoring test had 3/8 in. (9.5mm) diameter steel rebar embedded at the center of cylinder, and 1 in. (25mm) cover was maintained for the embedded rebar.

#### Measurements

### **Compressive Strength Test**

Mortar cylinders of size 2 in. x 4 in. (5cm  $\times$ 10cm) were prepared using cement and sand in ratio of 1:2.48, with a water-cementitious material ratio at (w/cm) of 0.4. Inhibitor admixtures in the amount of 1%, 2% and 3% by mass

of cement were added. They were then tested for compressive strength at 3, 7, 14, 28 and 56 days, in accordance with ASTM C109 [21] specification.

	Dagaga	Cement	Sand	Water	Admixture	Water reducer	
	Dosage	kg(lb)	kg(lb)	L(gal)	g(oz)	mL(in <sup>3</sup> )	
Peony Leave	1.00%	1.48 (3.263)	3.68 (8.113)	0.60 (0.159)	14.80 (0.522)	7.42 (0.251)	
	2.00%	1.48 (3.263)	3.68 (8.113)	0.54 (0.143)	29.60 (1.044)	7.42 (0.251)	
	3.00%	1.48 (3.263)	3.68 (8.113)	0.47 (0.124)	44.40 (1.566)	7.42 (0.251)	
Grass	1.00%	1.48 (3.263)	3.68 (8.113)	0.65 (0.172)	14.80 (0.522)	7.42 (0.251)	
	2.00%	1.48 (3.263)	3.68 (8.113)	0.63 (0.166)	29.60 (1.044)	7.42 (0.251)	
	3.00%	1.48 (3.263)	3.68 (8.113)	0.61 (0.161)	44.40 (1.566)	7.42 (0.251)	
Sugar	1.00%	1.48 (3.263)	3.68 (8.113)	0.65 (0.172)	14.80 (0.522)	7.42 (0.251)	
	2.00%	1.48 (3.263)	3.68 (8.113)	0.63 (0.166)	29.60 (1.044)	7.42 (0.251)	
	3.00%	1.48 (3.263)	3.68 (8.113)	0.61 (0.161)	44.40 (1.566)	7.42 (0.251)	
Dandelion	1.00%	1.48 (3.263)	3.68 (8.113)	0.65 (0.172)	14.80 (0.522)	7.42 (0.251)	
	2.00%	1.48 (3.263)	3.68 (8.113)	0.64 (0.169)	29.60 (1.044)	7.42 (0.251)	
	3.00%	1.48 (3.263)	3.68 (8.113)	0.63 (0.166)	44.40 (1.566)	7.42 (0.251)	
Control	-	1.48 (3.263)	3.68 (8.113)	0.67 (0.177)	-	7.42 (0.251)	

Table 1—Mix Proportion of mortar mixed with four green corrosion inhibitor and control sample

### **Rheology Test**

The rheology tests were used to characterize the fresh concrete mixtures. The K-slump and workability tests were performed on the samples in accordance with ASTM C1362 [22] to determine the effect of the green admixtures on the flow-ability, workability and the degree of compaction of fresh mortar.

### Setting Time Test

The setting times of the cementitious pastes were determined with a concrete penetrometer following the procedure set out in the ASTM C403 [23]. The point of initial set is reached when the penetration value is 500 pounds per square inch (psi).

### Water Absorption Test

Water absorption test in accordance with ASTM C1585 [24] was performed to evaluate the water resistance of the mortar specimens with three types of surface treatments. Before testing, all specimens were vacuum oven-dried at 60°C for 72 hours. After that, the specimens were moved to a sealable container at 23°C for 24 hours.

The test was performed by allowing one surface of the specimen to be in contact with water of 0.4 in. (10 mm) depth using a support. Using the supporting frame and keeping the water level at 0.04-0.12 in. (1-3 mm) above the top

of the support allowed continuous contact between the specimen surface and the water without changing the water depth throughout the test. The sides of the test samples were carefully sealed to create unidirectional flow through the samples. The weight of the specimen was recorded at fixed time intervals. The absorption coefficient ks (g/cm<sup>2</sup>· s<sup>1/2</sup>) was then determined using the following equation:

$$Q/A = k_{\rm S}\sqrt{t} \tag{1}$$

Where Q is the amount of absorbed water (g), A is the cross-sectional area of the specimen that was in contact with water  $(cm^2)$ , and t is the time (s).

#### Gas Permeability Test

Gas permeability test of concrete was conducted to evaluate the impermeability of the three types of surfacetreated concrete specimens. The test was performed using liquid methanol as the gas source to determine the gas transport properties. Specimens were vacuum oven-dried at 60°C for 72 hours to remove the moisture within specimen. Subsequently, the specimen was placed and sealed on the top of a cell with epoxy sealant to avoid any leakage of methanol vapor. The initial weight of the whole specimen setup including the cell, methanol liquid, specimen, and epoxy sealant was measured at the beginning of the test.

The values of mass variation versus time due to the vaporization of methanol liquid at a constant 60 °C water bath temperature during the test were continuously recorded at each time interval until a steady-state mass loss was reached. The gas permeability coefficient k ( $m^2$ ) was then calculated using the following equations.

$$p\nu = 10^{(8.0809 - \frac{1582.2}{239.76 + T})}$$
(2)

$$\eta = 10^{-7} (4.7169T^{0.618} - 99e^{-8.7593 \cdot 10^{-4T}} + 94e^{-7.916 \cdot 10^{-3}T} + 5)$$
(3)

$$Q = \frac{266 \cdot 10^{-3}m'}{10^{(8.0809 - \frac{1582.2}{239.76+T})}}T$$
(4)

$$k = \frac{2L\eta P_2 Q}{A(P_1^2 - P_2^2)}$$
(5)

where  $P_V$  is the absolute pressure of vapor (N/m<sup>2</sup>); T is the absolute temperature (K); g is the dynamic viscosity (N/m<sup>2</sup>); Q is the volumetric flow rate (m<sup>3</sup>/s); m' is the rate of mass loss (g/s); P<sub>1</sub> is the inlet pressure (N/m<sup>2</sup>); P<sub>2</sub> is the outlet pressure (N/m<sup>2</sup>); L is the length of the sample (m); and A is the cross-sectional area perpendicular to the flow direction (m<sup>2</sup>).

### **Corrosion Monitoring**

OCP, EIS and LPR tests were conducted for electrochemical corrosion analysis of green admixtures. The specimens were saturated in a NaCl solution with concentration of 3.5% and under freeze/thaw cycling. The EIS & LPR equipment used included PARSTAT MC multichannel potentiostat, a platinum electrode as counter electrode and an Ag/AgCl electrode as reference. By applying sinusoidal perturbations with a frequency from 100 kHz to 0.005Hz, the working electrode was polarized by  $\pm 10$  mV around its OCP and the current response vs. the applied voltage was

recorded to produce the EIS spectrum.

The LPR curves were measured within  $E_{ocp} \pm 20 \text{ mV}$  at a scan rate of 0.167 mV/s. Representing the slope of the polarization curve, the polarization resistance, Rp, can be calculated by:  $R_p=\Delta V/\Delta I$ (6)

Where  $\Delta V$  and  $\Delta I$  represent the voltage and current increments, respectively, in the linear portion of the polarization curve at i = 0. LPR measurements were used to calculate the corrosion current density by the Stern-Geary equation: icorr = $\beta_a\beta_c/[2.303(\beta_a+\beta_c)R_p]=B/R_p$  (7)

Where icorr is the corrosion current density,  $\beta_a$  is the anodic Tafel slope,  $\beta_c$  is the cathodic Tafel slope, and B is a constant related to  $\beta_a$  and  $\beta_c$ . In this study, a tentative value of 26 mV for the B constant was used.

### **RCM** Test

Follow the NT BUILD 492 [25], Two cylindrical samples in size of  $\varphi$  2 in. ×2 in. ( $\varphi$  50mm ×50mm) were sliced from the original mortar specimens in size of  $\varphi$  2 in. ×8in. ( $\varphi$  50mm ×200mm) at the age of 27 days for the RCM test (two specimens from each core, 0.4 in.-0.8 in. (10mm-20 mm) of the outermost surfaces of each core were cut off) and stored in water . One day prior to the RCM test, each series of the test samples was saturated with saturated limewater under vacuum conditions. The vacuum-saturation was performed following the procedure described in: surface-dry samples were placed vertically in a desiccator connected to a vacuum-pump and a pressure of 40 mbar was applied for 3 h. Then, with the vacuum pump still running, the desiccator was slowly filled with saturated limewater to immerse all the samples completely. After that, for an additional hour, the vacuum was maintained before allowing air to re-enter the desiccator. The samples were kept in the solution for about 18 h. The RCM test was performed on the saturated samples at the age of 28, 29 and 30 days. Power sources with constant voltage outputs (adjustable in the range of 0–80 V, accuracy of 0.05 V) were used. Four mortar samples were tested at the same time. The used volume of the catholyte (10% NaCl aq. solution) was about 14 L (3.70 gal) while the volume of the anolyte (0.3 M NaOH solution) was approximately 0.3 L (0.08 gal) per test specimen. The electrolytes were refreshed after each series of experiments. After the migration test, three mortar samples were split and sprayed with a 0.1 M AgNO<sub>3</sub> solution to determine the penetration depth of chlorides, while the total chloride concentration profile was measured on the fourth sample.

### **RESULTS AND DISCUSSION**

#### **Compressive Strength test**

Compressive strength values of specimens that have been cured for 56 days are given in Fig. 1. The peony leave group had the least side effect on strength, with an approximately 0.2% compressive strength reduction at 28 days when mixed with 1% PL-inhibitor. For both early age strength and long-term strength, the 1% added PL-inhibitor also had the minimum influence, with 8% reduction at 7 days and 4% reduction at 56 days. When more PL-inhibitor (3%) was mixed in the mortar, the strength decreased by 22% at 7 days, 7% at 28 days and 9% at 56 days. However, the dandelion group decreased the compressive strength by nearly 20% at 28 days when 1% D-inhibitor added into the mortar. The 28 days compressive strength of samples with 3% D-inhibitor also dropped 28% compared to the control group, which had the most significant side effect on mortar samples. The other two inhibitors (KG-inhibitor and SL-inhibitor) also reduced the compressive strength, but in an acceptable range. The reduction of compressive strength

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caused by different corrosion inhibitors was summarized in Table 2.

Compared to some green corrosion inhibiting admixtures for concrete, four types of inhibitors tested in this study had promising performance. For example, the 3% mixed calcium palmitate inhibitor was reported to reduce 50% compressive strength of concrete at 7 days and 40% at 28 days [26]. However, green corrosion inhibitors made of Bambusa arundinacea were proved to be able to improve the compressive strength at both early stage and long-term age [10]. Further studies can focus on the chemical mechanisms that reduce the strength of mortar mixed with these four green corrosion inhibitors, and the method to mitigate this strength reduction.



Fig.1—Compressive strength of mortar cylinders

	Peony Leave		Grass		Sugar Beet			Dandelion				
Dosage	1%	2%	3%	1%	2%	3%	1%	2%	3%	1%	2%	3%
3d	2.7	1.5	12.1	3.2	8.2	9.9	17.4	19.0	16.9	15.9	20.1	26.9
7d	8.2	14.2	22.2	14.3	9.3	11.0	18.9	20.0	22.2	20.3	24.3	32.8
14d	2.8	8.0	19.3	11.2	9.3	14.4	11.9	17.0	17.4	22.8	25.2	28.6
28d	0.2	4.6	7.3	10.2	9.6	13.5	7.0	3.1	14.8	20.8	23.7	28.1
56d	4.2	8.1	8.9	11.7	20.5	11.8	14.4	10.6	22.0	21.5	22.4	29.4

**Table 2**—Strength reduction of mortar samples

#### **Rheology test**

Workability change with time is also of significance in practice for transportation and casting of concrete before the initial set. The workability retention may be evaluated by the change in rheological parameters with time. K-slump values can reflect the flowability of fresh mortar or concrete.

The results of rheology properties are shown in Fig. 2 and Fig. 3. The control group had the K-slump value of 5.5 and workability value of 3.75. It shows that PL-inhibitor and KG-inhibitor could significantly increase the flowability and workability of fresh mortar. 3% added PL-inhibitor could increase the workability by approximately 1.5 and K-slump by 5. The 3% KG-inhibitor could improve the workability by 1 and K-slump by 0.8, approximately. However, D-inhibitor had a negative influence and reduced the workability by 40% and K-slump by 20%.

Compared with other admixtures improving the rheology of mortar and concrete, the PL-inhibitor and KGinhibitor are also competitive. Commercial available water reducer could potentially improve the slump by 40%. The ultrafine fly ash (UFFA), as a kind of mineral admixture which could partially replace the water reducer, was able to increase the slump by 6% maximum [27]. The series of polycarboxylic acid-based copolymers with block and graft groups of polyethlene oxide (PEO) chains could increase the slump by a maximum of 26% [28].

It is well-known that an increase in slump flow signifies greater deformability of fresh concrete and higher slump flow is generally the result of a reduction of the yield stress in fresh concrete [29]. Yield stress results of fresh concrete could be further used to shed light on the improved rheological behavior of mortar samples with the green admixtures incorporated [30]. Also, more experimental groups with different water/binder ratios could be explored to better understand the benefits of green admixtures.



Fig. 2—Workability of mortar samples



Fig. 3—K-Slump of mortar samples

### **Initial Setting time test**

Initial setting time is a parameter that showing the stiffening of the mortar and concrete. The initial setting time of four types of green admixtures with 1%, 2% and 3% by weight of cement are shown in Fig. 4. The control group's setting time was 357 minutes. Experimental results showed that all four green admixtures could increase the initial setting time of mortar. The sugar beet group had the most significant increase compare to other groups, almost increasing the initial setting time by 47% compared with the control group, when 3% SL-inhibitor. The dandelion group had the least impact on setting time, with only an approximate maximum 11% increase.

As the concentration of the green admixtures increased in the mortar samples, the settings times of mortar with PL-, KG- and SL-inhibitors increased significantly. On the other hand, the D-inhibitor only induced a relatively small increase in the initial setting time (Fig. 4).

The green admixtures used in this study also have the potential to be used as set retarders to slow the hydration of concrete for large or difficult pours in construction. Borogypsum, which is a newly studied set retarder in Portland cement, could increase the initial setting time by 32% [31]. Phosphogypsum, another widely investigated set retarder for cement could potentially triple the setting time of cements [32]. Triethanolamine (TEA), which is commonly used in concrete, has the potential to produce retardation of concrete initial setting by 44% [33]. Thus, green admixtures in this study, such as SL-inhibitor resulting in 47% increase in setting time, could be further developed as a commercial set retarder.



Fig. 4—Initial setting time of mortar samples

### **Transport Properties**

Water absorption and gas permeability are two important transport parameters related to corrosion. The rate of water absorption is closely related to the durability and service life of concrete which often goes through wet/dry cycling in the service. The higher the water absorption rate of the concrete, the more rapidly it is likely to deteriorate. Gas permeability has a close relationship to the chloride diffusion coefficient of concrete, which is an indicator of the risk of rebar corrosion in RC structures. Gas permeability is also related to the resistance of concrete to carbonation.

The water absorption rate and gas permeability coefficient are illustrated in Fig. 5 and Fig. 6. The experimental result indicated that the use of green admixtures had very little influence on these transport properties. Only the KG-inhibitor decreased the water absorption rate by more than 50%. However, the transport properties of mortar were not influenced significantly by other green admixtures, indicating that the samples with PL-, SL- and D-inhibitors added remain good resistance to the ingress of damage sources such as chloride ions or sulphate attacks. Microstructural analysis may be investigated to analyze the influence of green corrosion inhibiting admixtures on mortar samples. Hence, the threats of influence on properties of mortar or concrete could be mitigated.



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Fig. 6—Gas permeability of mortar samples

### **Corrosion Monitoring**

Fig. 7 shows the open circuit potential versus time of immersion in NaCl solution for the steel reinforcing embedded in the mortar samples mixed with the four types of green admixtures at two different dosages. All the OCP readings started within the low level of risk of corrosion, ranged from -33mV to -87 mV. After 3 days of immersion