

SELF-MENDING COMPOSITES INCORPORATING ENCAPSULATED MENDING  
AGENTS

## ABSTRACT

The present invention provides for a method, and compositions, of mending cement caused damaged by an external stress by incorporating microcapsules containing an aqueous mending agent into the cement matrix whereby the release of the aqueous mending agent is triggered by the stress that ruptures the microcapsule and the released aqueous mending agent mends one or more of the damaged cement properties. The aqueous mending agent encapsulated is one that does not require any additional factors such as catalysts or initiators and has a natural cement bond with an endogenous cement hydration by-product in damaged targeted area. The invention provides for added aspect of the cement matrix containing the aqueous mending agent microcapsules that reduces corrosion of the metal reinforcement material encased by the cement matrix. The invention additionally provides for a method of pretreatment of the metal reinforcement material at any time prior to the addition of the cement matrix to reduce corrosion in microcracks formed by external stress.

## BACKGROUND

Concrete is the most commonly used building material in the world. It is strong, durable, locally available and versatile. It is an inexpensive material to produce and is recyclable. Unfortunately, concrete is susceptible to many sources of damage. Cracks can form at any stage of its life and most begin internally where they cannot be seen for years until major repairs are needed. Damage is caused by a number of factors such as freeze/thaw cycles, corrosion, extreme loads, chemical attacks and other environmental conditions. Consequently, maintenance to concrete structures is frequent and costly. Billions of dollars are spent every year on buildings, bridges and highways for maintenance, making materials requiring less frequent repairs very appealing. In addition, the production of concrete is an energy-intensive process when mining, transportation and processing is considered. Its production level lies at about 2.35 billion metric tons per year and contributes an astonishing 10% of CO<sub>2</sub> emissions into the atmosphere.

Typically damage, deterioration and overall structural integrity are conventionally monitored through routine inspections and repair. This may involve a variety of approaches that includes one or more of the following: surface repairs, apply admixtures, sealant applications, surface washing and corrosion monitoring. In the past decade, the building industry has taken a

significant interest in engineering concrete as a “smart material” to alleviate the cost burden to maintain roads from excessive routine maintenance and excessive concrete production. The more conventional approaches have used chemical admixtures to limit the scale of damage. Humphrey et al (US Patent 7,513,948) incorporated branched hydrocarbons as part of a mixture of compounds that exhibited a higher degree of moisture resistance when cracks formed. In more recent inventions Li and Yang (US Application 12/104,637) embedded short polyethylene fibers to control crack width and extreme tensile ductility. Healing of microcracks of 50 um or less in width in the damaged material was accomplished by flowing water containing carbonates and bicarbonates into the crack which promoted the formation of calcium carbonate.

One invention to reduce microcrack damage is to use a method that reacts by a repairing cracks in a selective area. Nishiwaki et al used a heating device to melt small, film-like pipes that are embedded into the concrete when cracks occur as a method for repair. In yet another approach, Dry (US Patent 6,261,360B1 and US Application 11/932,899) incorporated glass pipes containing the cross-reacting agents such as polymerizable monomers and catalysts or two part epoxies into the concrete for self-healing capabilities. The major commercial limitation in the use of hollow-fiber or tubes as industry products is their infeasibility in the manufacturing, their ease of use and their cost effective deployment on scaled projects.

Similar to glass fibers methods, White et al (US Application 11/756,280) have developed a polymer composite system that incorporates a catalyst or activator and a polymerizable monomer into a microencapsulated polymer matrix. The healing agent is released upon crack propagation through the microcapsules, resulting in recovery of toughness after a fracture. This method has been used in variety of polymer composite systems. In another approach, Feng et al (US Application 12/863,670) used urea-formaldehyde resin polymer in microcapsules to provide self-healing through polymerization.

All of the prior methods used to promote self-healing of concrete or cement materials employ methods or compositions of material that act to produce polymeric or aggregate materials inside the microcrack to act as filler in the damage concrete or cement. In the present invention, the inventors have unexpectedly developed a novel method that produces a targeted self-mending process caused by a variety of stress factors whereby incorporated microcapsules are ruptured and release an aqueous mending agent that naturally and covalently bonds with the by-products of cement hydration in the damaged concrete resulting improving one or more

properties of cement as well as reducing corrosion of metal reinforcement incorporated in the cement.

## SUMMARY OF THE INVENTION

The present is directed to provide a method of mending cement damaged by an external stress by incorporating microcapsules containing an aqueous mending agent into the cement matrix that when released by an external stress mends one or more properties of the cement. More preferably, the invention is directed to provide a targeted release of the aqueous mending agent by rupturing of the microcapsule during the formation of a microcrack due to stress. Most preferably, the aqueous mending agent react with endogenous products of cement hydration in the damaged concrete to produce a natural cement bond that mends the damaged concrete.

In another aspect, the invention herein is directed to provide a method of reducing the corrosion of metal reinforcement incorporated in the cement for strengthening properties. A further aspect of the present invention is the treatment of metal reinforcement with aqueous mending agent microcapsules prior to the addition of the cement matrix.

In the first aspect of the invention, the cement matrix containing aqueous mending agent microcapsules when damaged by stress is able to improve at least one of the cement properties by at least 10% compared to the non-incorporated cement matrix, more preferably at least 25%, and most preferably at least 50%.

In the second aspect of the invention, the aqueous mending agent may be aqueous sodium silicate, calcium nitrite, calcium nitrite or any other mending agent that binds as natural cement bond to the damaged cement or combination thereof.

In the third aspect of the invention, the aqueous mending agent used in microcapsulation is a solution of 0.1 to 10% aqueous mending agent.

In the fourth aspect of the invention, the microcapsule material is a polymer, such as polyurethane, urea-formaldehyde polymer, a polystyrene or polymide, a gelatin, or any other material used to encapsulate the aqueous mending agent or combinations thereof.

In the fifth aspect of the invention, the external stress creating a microcrack and the targeted rupturing of the microcapsule in the microcrack region is caused by freezing, thawing,

loading, cracking, impacting, corrosion, weight, chemical, creep, expansion, shrinkage or combinations thereof.

In the sixth aspect of the invention, the aqueous mending agent microcapsule is added from 0.5% to 25.0% by weight of the cement mixture.

In the seventh aspect of the invention, the improved damaged cement property is one or more of the following; tensile strength, toughness, porosity, and water permeability.

In the eighth aspect of the invention, the cement matrix containing the aqueous mending agent microcapsules reduces corrosion of the metal reinforcement by at least 10% compared to the non-treated metal reinforced cement, more preferably at least 25%, and most preferably at least 50%.

In the ninth aspect of the invention, the metal reinforcement include, but not limited to, rebar or metal mesh of any type that provides for strengthening of the cement matrix. A further aspect of the invention includes any and all metals that are reactive to corrosion.

In the tenth aspect of the invention, the mending of the targeted area by released aqueous mending agent microcapsules reduces water transport through the concrete matrix due to reduced porosity, decreased interconnectivity and mended cracks will slow down the ingress of damaging chlorides, ultimately inhibiting the rebar corrosion rate.

In the eleventh aspect of the invention, the metal reinforcement may be pretreated with aqueous mending agent microcapsules at any time prior to the addition of the cement matrix.

In a twelfth aspect of the invention, the aqueous mending agent microcapsules may be produced, selected, and/or additionally treated to provide for enhanced the surface and physical properties of the microcapsules to adhere to the metal reinforcement. In a further aspect, the metal reinforcement may be treated to enhance its binding capacity or properties to the microcapsules.

In the thirteenth aspect of the invention, a composition of cement matrix containing a plurality of microcapsules and an aqueous mending agent in the microcapsules, whereby the microcapsules releases the aqueous mending agent upon stress.

In the fourteenth aspect of the invention, a composition of treatment metal reinforcement containing a plurality of microcapsules, an aqueous mending agent in the microcapsules, and

a metal reinforcement. A further aspect is the metal reinforcement is treated at any time prior to the addition of a cement matrix.

“Cement matrix” means any material containing cement materials including materials containing pebbles or rocks, such as concrete, and the incorporation of strengthening materials, not limited to fibers.

“Microcracks” means cracks that are between 10 to 400 microns in width.

“Self-healing” or “healing” means any agent that improves the properties of cement matrix upon release of the self-healing agent and may include a catalyst or activator that reacts with its self.

“Self-Mending” or “mending” means any agent that improves the properties of cement matrix upon release of the aqueous mending agent by bonding with endogenous hydration by-products of the damaged concrete and forming a natural cement bond.

## BRIEF DESCRIPTION OF DRAWINGS

The invention can be better understood with reference to the following drawing and description. The components in the figures are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

FIG. 1 represents adding microcapsules containing the aqueous mending agent into the concrete mix. After the load is applied, the mechanical stress ruptures the capsules, releasing the healing that can repair the cracks.

FIG. 2 is a light microscopy image of a polyurethane microcapsule synthesized through an interfacial polymerization.

FIG. 3 depicts a crack that propagates through the material directly to the center wire.

FIG. 4 represents load versus displacement (extension) for flexural strength characterization of control (a) and capsule-containing (b) samples.

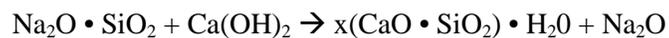
FIG. 5 represents open circuit potentials versus time for all corrosion and capsule samples in the electrochemical experiment.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention makes use of the discovery that an aqueous mending agent can be encapsulated into microcapsules and incorporated into a cement matrix, whereby upon targeted release from microcapsules caused by stress the aqueous mending agent reacts with endogenous products of cement hydration in the damaged concrete to produce a natural cement bond that mends the damaged concrete.

The novel method and composition presented herein provides for the production of aqueous mending agent microcapsules and use as an additive to a cement matrix. A targeted event producing a microcrack may be caused by a variety of stress factors that act as a trigger for self- mending process to occur in the localized region. Preferably, microcapsules containing an aqueous mending agent core are incorporated within the concrete matrix in the absence of any other additives, such as catalysts or activators, to promote or stimulate mending. When mechanical or other stress is applied, the microcapsules rupture releasing the aqueous mending agent into the microcracks formed by stress and the aqueous mending agent bonds with the damaged concrete improving at least one of its physical properties (FIG. 1).

In one example of the invention, sodium silicate reacts with calcium hydroxide, a product of cement hydration, and produces a calcium-silica-hydrate (C-S-H) gel – a binding material natural to concrete. An key aspect of the invention is that the mending agent resides in an aqueous environment within the microcapsule and the water facilitates the hydration of the damaged cement and subsequent bonding of the mending agent. The C-S-H gel ( $x \cdot (\text{CaO} \cdot \text{SiO}_2) \cdot \text{H}_2\text{O}$ ) fills the crack, and allows recovery of strength. The relevant chemical reactions are shown below:



C-S-H is a complex product that often has varying C/S ratios present and may differ slightly in nanostructure. It has been demonstrated in hydrated cement and is described as a network of nanoparticles. For this invention, only the first reaction forms the product rapidly. It is the newly formed C-S-H gel that will act as a binder and mender in cracks and pores, bridging the gaps in the material and ultimately improving its strength. The second reaction is a longer

time scale. Sodium-silica-hydrate (N-S-H) is observed in concrete as a result of the reaction between sodium hydroxide and silica. The long-term products initiated by the presence of the aqueous mending agent provides further integrity of the concrete.

In addition to sodium silicate, other mending agents include calcium nitrite and calcium nitrate.

In the production of microcapsules, White et al (US Application 11/756,280) and others have used a variety of methods for encapsulation of materials to generate microcapsules containing a self-healing agent or in this invention a self-mending agent. This invention is not limited to microcapsules, the aqueous mending agent may be delivered using hollow fibers used by Dry (US Patent 6,261,360B1 and US Application 11/932,899) or other shapes provided that the mending agent may be incorporated in the shape and that stress can be used to release the mending agent. In the present invention makes use of producing that have an outer diameter of 10 to 1000 microns. The desired properties of microcapsules may depend upon a variety of attributes that include, but are not limited to, resistance to aggregation, uniformly dispersed in cement mixture, temperature stability, long shelf life, encapsulate thickness, and resistance to mixing physical factors when added to the cement mixture.

The mixture for forming microcapsules containing a mending agent includes at least an aqueous mending agent solution, a surfactant, and a polymerizer. This invention preferably excludes the use of any other agents, catalyst or activators, or external stimulus that initiate the mending action. The mending agent solution is an aqueous solution of the mending agent having a concentration of 0.1% to 10% weight of mending agent per volume of water. Polymers used for production of microencapsules may include a polyurethane precursor such as a diol, a diisocyanate, and/or a monomer containing both alcohol and isocyanate functional groups. In other examples of polymers, the polymer precursor may include a urea-formaldehyde polymer precursor, such as urea and/or formaldehyde. In yet other examples of polymers, a polystyrene precursor, such as styrene and/or divinylbenzene; or a polyimide precursor, such as an acid chloride and/or a diamine. This invention is not limited to the microcapsules prepared as described herein and includes any and all materials regardless of composition and shape that provide for the containment of the aqueous mending agent that may be released upon stress.

Microcapsule properties such as the walls of the capsules or aggregation may be adjusted using ionic surfactant, such as a cationic surfactant, an anionic surfactant, or an amphoteric surfactant or non-ionic surfactant. Dispersing the mixture may use a variety of

protocols including mechanical agitation, magnetic stirring, vortexing, and high pressure jet homogenizing. Additional methods can be employed during or after the production of microcapsules to provide a more uniform diameter using either controlled processing or selection of microcapsules sizes using centrifugation, sonication or other post-production methods.

The present invention incorporates aqueous mending agent microcapsules into the cement matrix by blending microcapsules into the wet cement mixture that constitute between 0.5% to 25.0% of the total weight. The aqueous mending agent microcapsules may be added initially or just prior to pouring the cement mixture into the molded article.

Preferably, the incorporation of the aqueous mending agent microcapsules restore at least one of the cement properties at least 10% compared to the non-incorporated control cement, more preferably at least 25%, and most preferably at least 50%.

The present invention further provides for reducing the corrosion of metal reinforcement incorporated in the cement for strengthening properties. Examples of metal reinforcement include, but not limited to, rebar or metal mesh of any type that provides for strengthening of the cement matrix. Metals include any and all metals that are reactive to corrosion. When stressed, the mending agent is released and some of the aqueous mending agent deposits on the metal reinforcement bars (rebars) traditionally used in concrete. The formation of a passive film on the surface of the metal will provide protection of the metal reinforcement from corrosion. Additionally, the mending of the targeted area will reduce water transport through the concrete matrix due to reduced porosity, decreased interconnectivity and mended cracks will slow down the ingress of damaging chlorides, ultimately inhibiting the rebar corrosion rate. Preferably, the cement matrix contained the aqueous mending agent reduces corrosion of the metal reinforcement by at least 10% compared to the non-treated metal reinforced cement, more preferably at least 25%, and most preferably at least 50%.

A further aspect of the present invention is the treatment of metal reinforcement prior to the addition of the cement matrix. Microcapsules may be produced, selected, and/or additionally treated to provide for enhanced surface and physical properties to adhere to the metal reinforcement. Further, the metal reinforcement may be pretreated to enhance its binding capacity or properties to the microcapsules. Preferably, the treatment of the metal reinforcement reduces corrosion by at least 10% compared to the non-treated metal reinforced cement, more preferably at least 25%, and most preferably at least 50%.

#### Example 1: Production of Polyurethane Microcapsules.

The *in situ* synthesis using an interfacial polymerization was adapted from Saihi *et al.* is described in the following steps. 4.202mL of Span 85 and 2.116mL of polyethyleneglycol (PEG) were dissolved in 90mL of toluene. A 15mL aliquot was taken from this solution and placed into a separate beaker (referred to as E<sub>1</sub>). 0.682mL of methylene diisocyanate (Basonat) and 0.0469mL of dibutyl tin dilaurate was dissolved in E<sub>1</sub>. This blend was mixed at 350 rpm to ensure a homogenous mixture and set aside. The original mixture (Span 85, PEG and toluene) was combined with 30mL of water, stirring at 8000 rpm in a homogenizer or blender. Finally, E<sub>1</sub> was added to this primary emulsion and stirred at 700 rpm for 10 minutes at room temperature. The speed was reduced to 350 rpm at 63°C and allowed to react for 4 hours. An optical microscope image of a polyurethane microcapsule is shown in FIG, 2. Microcapsules sizes varied in size from 40-800 microns.

#### Example 2: Production of Concrete Samples.

Concrete samples were prepared to the specifications of ASTM C-109 with a mix containing 1375 grams of Ottawa C-109 sand, 500 grams of Type I/II Portland cement and 242 mL of water. For samples containing the polyurethane microcapsules, the capsules were added to the mix water at 2% volume and prepared identical to the control samples. Molds of dimensions 160mm x 40mm x 20mm (for flexural strength) and 500mm x 500mm x 500mm (for compressive strength) were used. After being stripped from the molds, the specimens were submerged in water for two days then contained in a 95% constant humidity environment for 28 days to ensure full curing.

#### Example 3: Testing Protocols.

For mechanical strength test, randomized internal microscale damage was induced with an applied load to incipient failure, to mimic realistic cracking patterns. For the corrosion testing, one large crack was induced directly to the iron wire to ensure a common path between samples.

For the flexural strength tests, approximately 160mm x 40mm x 20mm samples were used. Each sample was subjected to an applied load of 0.25 mm/min to induce microcracking within the sample. The cracking was minor and internal only and meant to mimic microscale damage and deformations that occur within the concrete after applied or natural stress, and prior

to catastrophic failure. After one week, these samples were retested to see how much strength has been recovered after the initial damage.

For the corrosion experiments, a larger, single crack was induced to give the sodium chloride solution a direct and common path to the iron wire in each sample. This was achieved by subjecting the 160mm x 40mm x 20mm samples to a three point bend test so that a crack propagated directly to the wire upon failure. An example of a representative sample with a crack is shown in FIG. 3.

#### Example 4: Testing of Compressive Strength.

The experimental procedure to determine the compressive strength of each specimen was adapted from ASTM C109 (Allen RF et al, Annual Book of ASTM Standards, p71). Each sample is centered between the two parallel discs. The strain rate is 1 mm/min. For the first test, the load is stopped after the sample has reached a maximum load and shows a gradual descent, but is not allowed to reach failure. After the short term mending time has passed, each sample is retested to failure. Only the results of the retested samples are presented herein.

The results of the compressive strength re-test for 5 control samples and 5 samples containing microcapsules are presented in Table 1. No loss was found in compressive strength for the capsule-containing samples.

Table 1. Compressive Strength in Control and Microencapsulated Samples.

Sample	Control, strength (ksi)	With 2% vol. microcapsules (ksi)
1	2.279	2.253
2	2.283	2.307
3	2.247	2.875
4	2.244	2.579
5	2.276	2.718

The microcapsules proved to be a highly effective way of encapsulating the mending agent for a targeted release. The results from the compressive strength tests show that the capsules do not interfere with the cementitious matrix.

#### Example 4: Testing of Flexural Strength.

The experimental procedure to determine the flexural strength of each specimen was adapted from ASTM C348-97 (Allen RF et al, Annual Book of ASTM Standards, p203). The flexural strength was measured by means of a three-point bend test. Samples were supported by two parallel beams and compressed by one central beam. The load was set to move at 0.25 mm/min. For the first test, the load was stopped after the sample had reached a maximum load and showed a sharp descent, but was not allowed to reach failure. After the mending time had passed, each sample was retested to failure.

The subsequent experiment was used to evaluate whether the material was able to recover some of its strength after acquiring some minor, microscale damage. First, the sample was loaded to incipient failure, indicated by the sharp decrease in the load-displacement curve. The samples were then left to mend for one week. During this time period, the aqueous mending agent that was released from the capsules had time to react with the calcium hydroxide to form the C-S-H, filling some of the cracks that have formed. The results for 5 control samples and 5 samples containing the microcapsules are shown in Figures 4 and summarized in Tables 2 and 3.

Table 2. Flexural Strength in Control Samples.

Sample	Initial Max Load, N	Max Load After Damage, N	Recovered, %
1	512.9	46.7	9.11
2	490.7	57.6	11.7
3	541.9	76.6	14.1
4	470.6	66.4	14.1
5	525.8	69.6	13.2

Table 3. Flexural Strength in Microencapsulated Samples.

Sample	Initial Max Load, N	Max Load After Damage, N	Recovered, %
1	495.7	124.4	25.1
2	416.7	85.9	20.6
3	476.6	125.2	26.2

4	513.8	127.5	24.8
5	528.2	130.5	24.7

Strength recovery was reported as a percentage of the maximum strength reached after minor damage has been induced compared to the maximum strength in the initial test. The control samples had about 10-14% of its initial strength left after microscale damage had occurred. The samples containing the microcapsules restored 20-26% its flexural strength after the damage. Compared to control samples, the aqueous mending agent microcapsules restored 43% to 260% more of cement flexural strength. This was indicative of the capsules rupturing where the cracks were initiated, partially mending them and providing more strength to the samples in the second test. Ultimately, this type of mending is desired to promote a longer life of the material since it is prolonging the time to failure.

The area under the stress-strain curve was obtained to provide a measure of the toughness of the material and is summarized in Tables 4 and 5. Compared to the average of the control samples, concrete samples containing the aqueous mending agent microcapsules restored 85% more of cement toughness.

Table 4. Toughness of Control Samples.

Control	Toughness (N-mm), initial damage	Toughness (N-mm), Failure
1	31.5	11.6
2	24.0	4.6
3	42.6	20.1
4	28.9	7.8
5	31.5	11.8
Average	31.7	11.2

Table 5. Toughness of Capsule-Containing Samples.

Capsule	Toughness (N-mm), initial damage	Toughness (N-mm)s, Failure
1	35.9	24.4
2	27.4	14.9
3	22.6	20.8
4	34.1	21.2
5	39.9	22.9
Average	31.9	20.8

High strength concrete exhibits a brittle behavior in which cracks quickly propagate. This was displayed in the initial test of the flexural data in which a linear relationship was interrupted by a sharp decrease in the load (FIG. 4). After the initial damage has been done, the material exhibits a much more ductile behavior. This was more evident in the capsule-containing samples, and results in higher toughness than the controls.

A critical ability of the invention was demonstrated in testing the flexural strength after inducing microcracks, where the presence of the microcapsules restored the material performance by at least 10% compared to the control samples.

#### Example 4: Testing for Corrosion Inhibition.

A 0.5M solution of sodium chloride was used to represent the ingress of chlorides to the steel reinforcement bars in concrete. An acrylic well was adhered to the surface of each rectangular sample with 3M 5200 Adhesive Sealant to ensure a tight, waterproof seal. The cylindrical well is 3 centimeters in diameter and was located directly over the wire present at the center of each sample. The bottom face opposite the well was fixed with a piece of Parafilm and all other surfaces were sealed with duct tape. A piece of sandpaper was used to sand off any rust or impurities that may have built up on the iron wire during curing and to ensure a good connection of the voltmeter to the wire. A potassium chloride reference electrode was placed in the empty well. The sodium chloride was poured into the small well and allowed to travel

through the pores and crack to reach the iron wire. The voltage of the wire was recorded over time until the wire was corroded internally.

The most common and routine inspection of reinforced concrete was used to monitor the open circuit potential of the rebars to monitor and detect corrosion. A potential higher than -0.200V implied a low risk of corrosion. If the potential was between -0.200V to -0.350V, it was an intermediate level of corrosion. If the potential drops below -0.350V, there was a high risk of corrosion. Finally, reaching a potential of -0.500V was indicative of severe corrosion. For the results presented here, each sample was subjected to the sodium chloride solution until it displayed severe corrosion, or the potential reached -0.500 volts. A summary of the results is shown in FIG. 5.

A rapid decrease in potential was observed when the sodium chloride was first poured into the well. In less than 40 seconds, each of the control samples had reached a potential near -0.350V, which indicated there was already a high risk of corrosion to the wire. Control 1, 2 and 3 lasted 96s, 118s and 212s, respectively, after which they all were severely corroded.

Capsule samples 1, 2 and 3 also showed a rapid decrease in potential initially, similar to the control samples. The potential reached -0.350V in 86s, 30s and 40s, respectively. Beyond this point, however, the capsule containing samples showed a significant difference from the control samples. The potential was sustained at this intermediate corrosion level. The voltage very gradually decreased to -0.400V in 276s, 200s and 124s, respectively. The time taken for these samples to reach a voltage of -0.500 volts was indicated in the figure. Capsule sample 3 exhibited the shortest time period, going from -0.400 to -0.500 volts in 15.6 minutes. Capsule sample 2 followed with 18.5 minutes until severe corrosion and finally, the first sample lasted the longest with 19 minutes of elapsed time before severe corrosion was observed. The key observation was a significant retardation in corrosion in the capsule containing samples.

Two mechanisms for corrosion inhibition are proposed. The first involves the formation of a passive layer to protect the metal. In the second, the ruptured capsule would fill the cracks and reduce porosity and interconnectivity to decrease the solution inhibition rate. The initial corrosion rates were very similar, shown by a sharp, sudden decrease in the potentials of each sample. The control samples exhibited uniform corrosion. The chlorides permeate through the concrete quickly and severe corrosion is observed. The capsule-containing samples were able to sustain the intermediate potential. This behavior was explained by a combination of both the mending properties and passive layer. First, there was a presence of a thin passive layer that

formed from the effects of the ruptured capsules. The chlorides moved quickly through the path of least resistance, which was the large, induced crack directly to the wire, and affected any of those areas not protected by the passive film. These areas would be easily corroded, explaining the similarity in the initial corrosion rate and potentials. With some passive layer present, however, it would take the chlorides longer to have a similar affect on the wire compared to the control samples, which explains why the time taken for the potential to reach the intermediate level of corrosion at -0.350 volts was longer.

The results for the capsule-containing samples showed a significant amount of corrosion inhibition compared to the control samples. With increased capsule loading (optimized for strength), more silicates can be deposited onto the wire to form a passive layer that could protect it for greater time. An added approach is the pre-treatment of metal reinforcement with microencapsulates optimized for adherence to the metal reinforcement surface. An ideal application for this system would be as an added aid for corrosion inhibition in an already protected structure.

## WHAT IS CLAIMED:

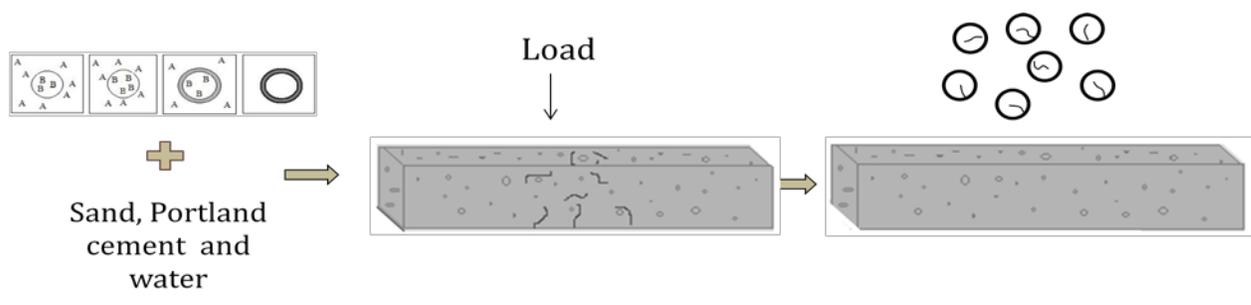
- Claim 1: A method for mending cement damaged by a stress comprising; encapsulating an aqueous mending agent within a microcapsule, adding the aqueous mending agent microcapsule to cement matrix, pouring the cement matrix containing the aqueous mending agent microcapsule into a form, releasing the aqueous mending agent microcapsule by stress, forming a natural cement bond, and improving at least one property of the damaged cement.
- Claim 2: The method of claim 1, wherein the aqueous mending agent is selected from a group consisting of aqueous sodium silicate, calcium nitrite and calcium nitrite.
- Claim 3: The method of claim 1, wherein the aqueous mending agent is a solution of 0.1 to 10% mending agent.
- Claim 4: The method of claim 1, wherein the microcapsule is selected from a group consisting of polyurethane, urea-formaldehyde polymer, a polystyrene, polyimide and gelatin.
- Claim 5: The method of claim 1, wherein the stress is selected from a group consisting of freezing, thawing, loading, cracking, impacting, corrosion, weight, chemical, creep, expansion, and shrinkage.
- Claim 6: The method of claim 1, wherein the damaged cement property is selected from a group consisting of tensile strength, toughness, porosity, and water permeability.
- Claim 7: The method of claim 1, wherein the mending microcapsule is added from 0.5% to 25.0% of cement mixture.
- Claim 8: The method of claim 1, wherein the cement matrix containing the aqueous mending agent microcapsule is poured into a form containing a metal reinforcement.
- Claim 9: The method of claim 8, wherein the aqueous mending agent reduces corrosion of the metal reinforcement by releasing the aqueous mending agent microcapsule by stress.
- Claim 10: A method for reducing corrosion by treating the metal reinforcement with aqueous mending agent microcapsule prior to pouring the cement matrix with or without aqueous mending agent microcapsule into a form.

Claim 11: The method of claim 10, wherein the metal reinforcement is pretreated to enhance its binding capacity or properties to the aqueous mending agent microcapsule.

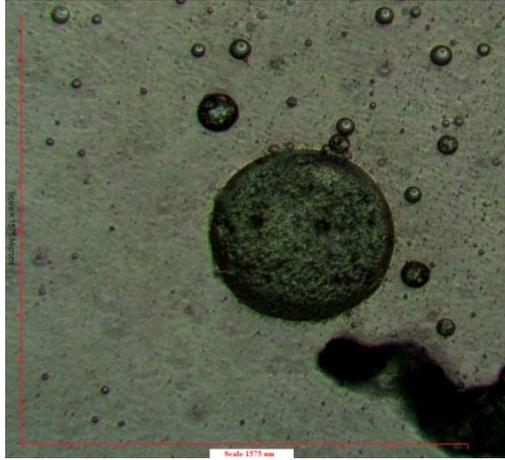
Claim 12: A composition for mending cement damaged by a stress comprising; a plurality of microcapsules and an aqueous mending agent in the microcapsules, wherein the microcapsules release the aqueous mending agent upon stress.

Claim 13: The composition of claim 12 for reducing corrosion, wherein the cement matrix containing the aqueous mending agent microcapsule is poured into a form containing a metal reinforcement.

Claim 14: A composition for reducing corrosion of metal reinforcement, wherein the metal reinforcement is treated with aqueous mending agent microcapsules prior to pouring of the cement matrix.



**FIG. 1**



**FIG. 2**



**FIG. 3**

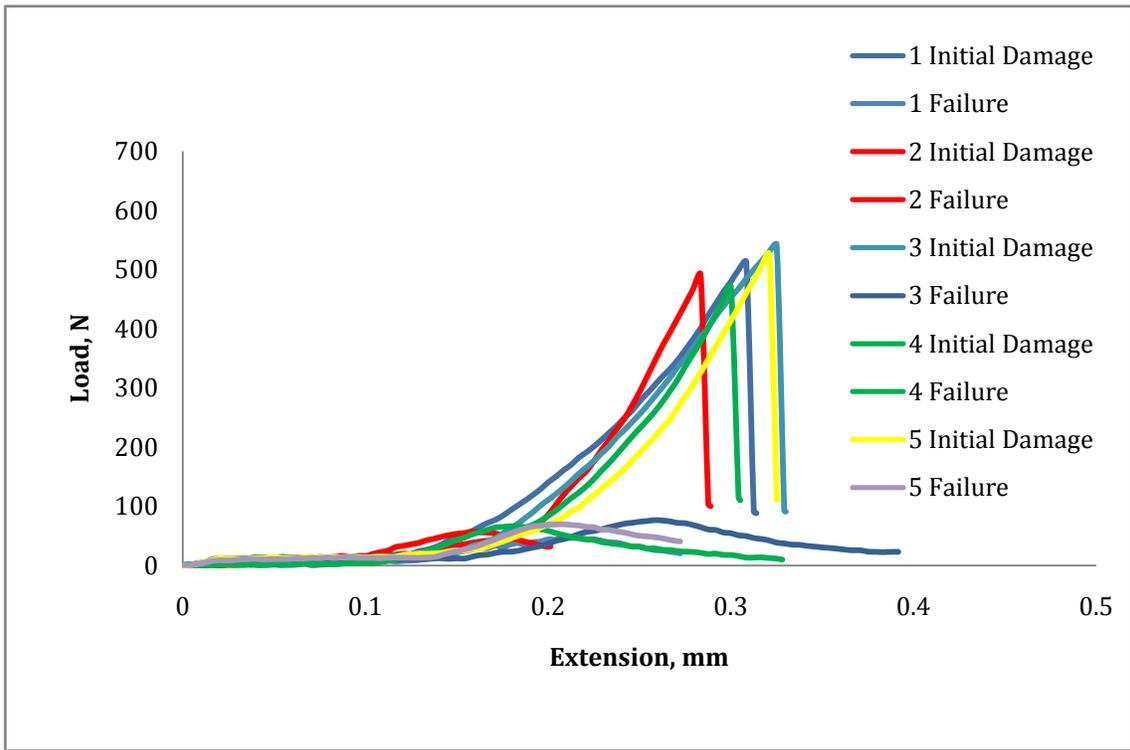


FIG. 4a

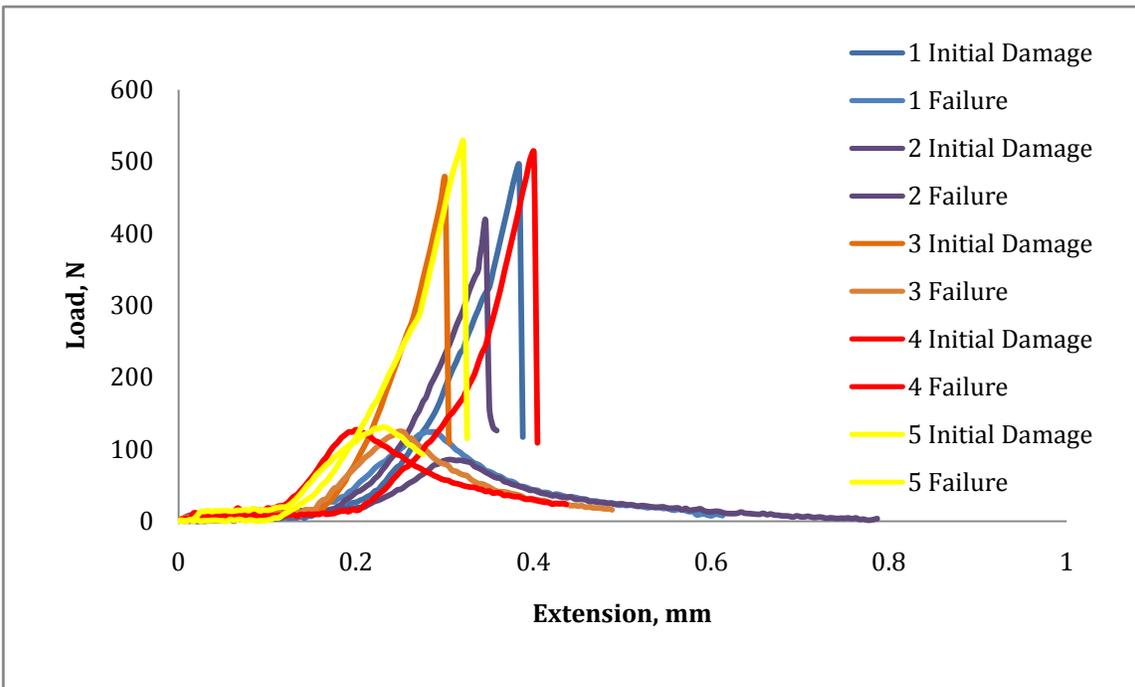


FIG. 4a

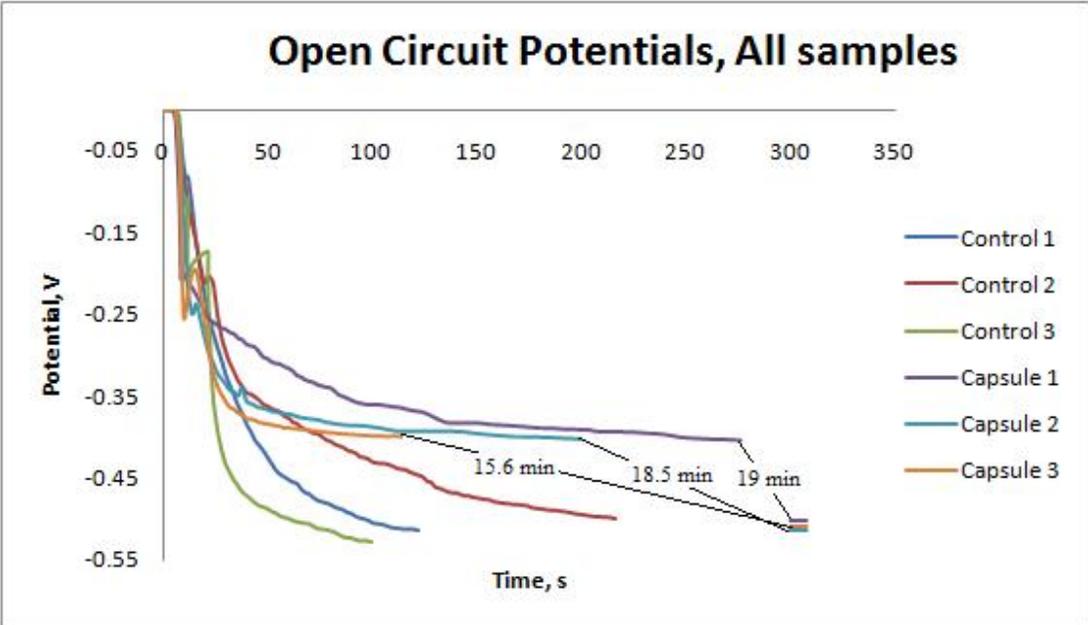


FIG. 5

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