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Steel Microstructure and Compressive Strength in Mortar When an Electrochemical Chloride Extraction is Applied

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Abstract: The focus of this paper is to examine and review how applications of Electrochemical Chloride Extraction (ECE) affect the mortar mechanical properties. The mortar specimens were prepared with water/cement (w/c) ratio of 0.5 and contaminated with 5% of NaCl by mass of cement. A clean steel rod was centrally embedded in each specimen. The electrochemical treatments were based on different electrical current densities of 1, 3, 6 and 9 A/m^2 that were applied for 15 days. The state of corrosion was monitored before, during and after applying ECE regularly for two weeks. Selected samples from the cover zone of the untreated and treated specimens were taken to assess their chloride profiles. Despite being a slight change in the microstructure at the surface of the steel rod when this technique was applied (high current densities), the results of the compressive strength on mortars were not affected by ECE.

Key words: Corrosion, Chloride, Mortar, Microstructure, Compressive Strength

1. Introduction

For a long time, the most widely used material for construction has been concrete, whose consumption has exceeded all building materials put together 1. Although many people believe that Reinforced Concrete Structures (RCS) do not have any problems of degradation, one of the most important causes of deterioration of these structures is the corrosion of reinforcing steel 2. This issue has been a great interest in the last three decades, for the reason that the cost of repairs are extremely high and sometimes higher than their initial construction cost 3.

Under normal conditions, concrete is capable of providing protection to reinforce steel against corrosion. It's because of high quantity of alkalinity that has a pH in the range of 12.5 to 13.5 in the concrete. In a highly alkaline environment, the steel creates a thin continuous and adherent film on its surface. This thin film prevents the dissolution of the iron itself 4. However, the durability of the RCS can be reduced by a corrosion attack. The factors that bring about the corrosion in the RCS are.

- Aggressive ions (chlorides, sulfate and sulfides) which have to exceed a critical threshold of concentrations 5.
- Concrete Carbonation 6.

The conventional techniques of repairing concrete can assure the elimination of the carbonated concrete and contaminated concrete by chlorides; however, the conventional way of patching concrete does not solve this type of deterioration, because it is very difficult to remove the all contaminated concrete 7. For that reason, there were created Electrochemical Rehabilitation Methods (ERM); and one of those methods is the Electrochemical Chloride Extraction (ECE) 8-11. Even though this technique can remove large amounts of chloride from concrete it is important to study the side effects that it causes in the steel rod and on concrete itself, since there is only a small amount of research done about this issue. Nzeribe *et. al.* found that using the ECE (with current densities lows) reduces the amount of chlorides inside the concrete. However, they found negative effects too, such as the

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reduction of mechanical properties of the concrete, but they do not mention the damage done quantitatively12. This article has an objective of making a comparison of the mechanical properties before, during and after a ECE, that is was done on concrete and a steel rod. The treatment was applied on different current densities of (1, 3, 6, and 9 A/m^2) during 15 days.

2. Experimental

2.1. Materials used

To produce the mortar specimens, a type of Portalnd Cement Compoud (CPC) 30R was used, with a ratio of cement/sand/water of 1/3/0.5. The mortar was contaminated when it was prepared with a sodium chloride (NaCl), a 5% of the relation of cement weight. The mortar specimens were made in a cylindrical shape with a diameter of 10 cm and a length of 20 cm. These specimens were cast, compacted and cured according to the ASTM C 192/C192 13. In the center of the mortar specimen a steel rod was introduced that was previously cleaned in a solution of hydrochloric acid (HCl) of 50% and 4 grams/liter of hexamethylenetetramine was added as an inhibitor. The diameters of the steel rods were 0.9 cm, the total length was 10 cm long and its exposed length was 7.5 cm. Once specimens were cast and then stored in a curing room al 20°C and RH of 95% for 24h. Following this period, the specimens were demoulded cured at 20 +/- 1°C and RH of 100%. After the curing period, ten mortars were exposed to the aggressive solution and the exposure time began into account; one cylinder was used as a test subject to obtain the compressive strength of the mortar without inserting a steel rod. Three of the once mortars were used for electrochemical testing and compression testing but without ECE. Finally, in the last seven cylinders, it was carry out an ECE during 15 days, at different current densities of 1, 3, 6, 9 A/m^2. The compressive strenght results obtained, according to ASTM C 39 13. In table 1 summarizes Mortar specimens that have been previously contaminated with NaCl, shows the current densities used in the experiment.

(Table 1 here)

2.2. Electrochemical tests

In order to obtain Ecorr values (potential corrosion in a open circuit) and PR (polarization resistance), one steel rod that was contained inside the mortar was used as a work electrode, an external rod was used as a counter electrode; a Saturated Calomel Electrode(SCE) was used as a reference electrode. The behavior of the corrosion on the steel rod was monitored before, during and after application of the ECE. The calculation of the corrosion rates (i_{corr}) lets us know the active or passive state of reinforced steel quantitatively. In order to obtain these values (i_{corr}) the equation of Stern and Geary was used 15, 16.

2.3. Application of the ECE

Seven specimens that were previously contaminated with chloride ions (Cl^-), were covered with a soft piece of cloth that it was moistened in a saturated solution of calcium hydroxide ($Ca(OH)_2$), and a steel mesh was placed on top of the soft piece of cloth. Each steel rod that was contained inside the mortar was connected to a negative terminal of a power supply, so that the steel reinforcement acted as a cathode; at the same time, the steel mesh was connected to the positive terminal of the power supply, which acted as the anode. The electrical current density delivered on the steel rod surface was 1, 3, 6 and 9 A/m^2. The periods of this application of the extraction lasted 15 days.

In general, the methodology applied consisdered also an external cathode short-circuited with the rebar and located on the concrete surface oppsosite to the anode 17. After the treatment was finished, the electrochemical response of the rebars was periodically measured to valuate the effectiveness of the treatment and the ability of repassivation of the rebars. Figure 1 shows the image of the mortar cylinders assembly during the ECE. During the connection of the electric field the current density passed through the rebar was monitored with a data-logger.

(Figure 1 here)

3. Results and discussion

3.1. Chloride Analysis

The chloride analysis was carried according to ASTM D 512 11 in aqueous extracts of mortar, using $2Hg(NO_3).H_2O$ solution and bromophenol blue-difenilcarbazone as indicator. All experiments were performed three times and the results are reported as an average value.

The visual inspection of the rebar shows a free-oxides surface, without any sign of corrosion, confirming the efficiency of the treatment. Figure 2 summarizes the results of the remaining amounts of total chlorides for the cylindrical mortar specimens, one with the ECE at 1 A/m^2 and the other without the treatment. Observe the differences in the amounts of chloride that were removed when the ECE was applied. The reference was taken based on the mortar cylinder that had no treatment, free of chloride. By using the extraction it was possible to decrease the amount of these ions, the amount left behind was 73% after a 15-day treatment, therefore it was reduced 27%.

(Figure 2 here)

The same figure shows that by increasing current density in the treatment it also increases the amount of chloride extracted from the mortar. Nzeribe *et. al.* conclude in one of their works that, there is a difference in the reduction of chloride ions. When the samples are treated with a current density of 1 A/m^2 compared to the samples that were treated with 3 A/m^2. The total reduction of ion Cl- content was about 26% at 1 A/m^2 and 48% at 3 A/m^2 12.

Researchers have found high efficiencies of chloride removal were obtained by this method with the rebar connected to the cathode during the treatment: an efficiency of the chloride removal treatment of 75% was reached when the simultaneous application of nitrite was considered, while an efficiency of 55% where obtained with the conventional treatment of chloride removal without simultaneous introduction of nitrite 18.

3.2. Corrosion Potential.

Figure 3 summarizes the evolution of Corrosion potential during the entire experiment. Before starting the treatment, all Corrosion potentials were at a 90% of probability of corrosion. After carrying out the ECE (with different current densities), the corrosion potentials were polarized holding values from -800 to -1200 mV in reference to SCE. In the region of 0 to 15 days (period of the ECE) it could be observed that the specimen that was given the higher current density (9 A/m^2) presented a higher alteration in the Corrosion potentials. This might be due to the high supply of energy to the electrodes in steel rod, which caused these variations. Assessment of the short-term efficiency of ECE on the corrosion rate of corroded reinforcement is preferable to be carried out after a short period from halting ECE process (about 4 weeks) and not immediately after halting the treatment, earlier study carried out by Abdelaziz et al. 19.

(Figure 3 here)

After the treatment was finished, we waited enough time so that the corrosion potentials were stabilized. The waiting periods were 30, 40 and 55 days for the specimens to which a current density of 3, 6 and 9 A/m^2 was applied, accordingly. Finally, after completing the test, the corrosion potential measurements were placed in a region of probability of uncertain corrosion (-350 mV), such a way that is possible to concluded that if the specimens had been monitored for a longer period of time, corrosion potentials could be much more positive and possible to passivate the steel using this technique, which some authors have argued 1921.

In the same chart it shows a specimen which began with the same degree of corrosion than previous ones, but this sample was not exposed to ECE, It also shows that during the test, the specimen is placed in a region of high corrosion, so the ECE is positively affected in the degradation of the steel, with respect to a specimen that has no treatment 22.

Andrade 19 explained in one of her works that the ECE can achieve repassivation of steel, even when the steel rods with corrosion potential start of at -600 mV and corrosion rates until reaching 0.2 $\mu A/cm^2$. She reported that after to the ECE and three years of monitoring, all corrosion potential values were more positive (-200 mV) and with corrosion rates (less than 0.1 $\mu A/cm^2$) placing the steel in a typical passivity values. Andrade suggests that a decisive factor in achieving efficient ECE is the relationship of load versus resistance, known as Standardized by the Resistance Charge (SRC) and must have a value of at least 1800 $Ah/m^2 k\Omega$. (10). For this test, the SRC values obtained were above 1980 $Ah/m^2\ k\Omega$, so it is possible that if these samples were monitored for at least one year, the armors will be placed in a passivity zone due to the application of ECE. After ECE, visual examination of the steel surface revealed a fine white product similar to the product reported in the other works 1023,24. Also was found black magnetite, around steel without ECE treatment, has been reported 925.

3.3. Microstructure of the steel rod

The following microstructures were obtained from the cross section of the steel rods under different experimental conditions, based on Table 1. The micrographs were taken under an optical microscope (OM). The images shows that the steel rods have a homogeneous composition of ferrite (white dots) and perlite (black dots). The corrosion products can be distinguished as a dark dense layer adherent to the rods, inside this layer there is a continuous white zone compared to the internal part of the rod. With regard to the microstructure of the rod in Figure 4, this specimen was contaminated with chlorides, without undergoing an ECE treatment. The average distance obtained in this area was 45 µm.

(Figure 4 here)

According to Figure 5 and Figure 6, the rods were subjected to contamination of chlorides with a subsequent extraction, during 15 days of treatment by applying 6 and 9 A/m^2 respectively. It can be observe an increase in the white zone (possibly a reduction in the amount of perlite), based on the increased current density, giving radial values from 79 µm to 104 µm.

(Figure 5 here)
(Figure 6 here)

The steel rods that were exposed a ECE with high current densities, have a slight decrease in the amount of perlite at the periphery of the cross section, known as decarburization process. Marcotte 26 mentioned that the ECE can cause a reduction of oxygen at the steel / mortar interface , causing an alkaline attack on the steel surface.The possible answer to this change in microstructure on the periphery, is attributed to the extraction process that requires energy for migration of species. As this energy increase it may also occur a greater alteration in the microstructure. This in turn, can lead to a reduction in the amount of perlite at the surface the in these microstructures. In table 2 summarizes the radial thickness at the periphery of the steel rod(white area) under different conditions.

(Table 2 here)

Figure 7 shows an Energy-dispersive X-ray spectroscopy (EDX) analysis done on the products of corrosion of the rod with ECE performed. It also found characteristic elements of the steel, it is noteworthy the presence of calcium ions. The calcium that is present in the corrosion products can be attributed to the migration of species during the ECE. since this is a positively charged ion, was attracted to the steel rod 26. Other studies found, that there is a high accumulation of crystals of $Ca(OH)_2$ in the steel-concrete interface during the ECE, of which, the presence of calcium on the surface of steel awarded to the compound 27.

(Figure 7 here)

3.4. Compression tests of mortars

In table 3 the results of compression tests of mortar specimens with different testing conditions are summarized. It also shows that the compressive strength in all specimens was much higher than expected, (compression strength = 510 Kg/cm^2, with 28-days setting time). The reason is simple; it's because the setting time for the samples was three times longer than the required time, so the result was an increased compression strength for the mortar.

(Table 3 here)

Something important to mention about this investigation, is the increase that was achieved with the average compression resistances when the treatment was applied. The specimen that acted only as a reference had a Compressive Strength (σ_c = 522 Kg/cm^2), for those samples that did not receive the ECE a $\sigma_c \approx 576$ Kg/cm^2 was reached, and finally for the samples with ECE, its $\sigma_c = 600$ Kg/cm^2.

The mechanical resistance augmentation that was obtained on the specimens with the ECE and without the ECE was, because the mortar specimens were dim while the electrochemical measurements were acquired, it's possible that by increasing the time of forge, the resistance to compression was altered in a positive way. Finally, the NaCl that is presented in the reinforced concrete is very well known to provoke harmful effects in mix. The prolonged periods of exposure influence in a negative way the mechanical resistance on the rod. However, by obtaining the results in table 3 and comparing the contaminated specimens with NaCl (1-9) with the specimens that do not have Chlorate (specimen cero) a very small difference is observed in the compression to resistance, showing a greater resistance to compression with the specimens that were contaminated with NaCl. This slight increment can be attributed to the NaCl (which behaves very similar to $CaCl_2$) for a short time cure; these substances will increase the resistance of concrete and on mortars 28. In the work published by M. Nzeribe Ihekwaba, he found that the compressive strength in concrete varies slightly with current density used. When it is applied to the experimental current density of 1 A/m^2 its σc gives values of 44.7 MPa, and with the increase of 3 A/m^2 the result is 44.2 MPa. The paper explains that the application of low current densities (1A/m^2) the affect on the macro structure of the cement paste is mild 12. With respects to this experiment, when using high current densities, the effects on mechanical properties changed very slightly.

Figure 8 shows the plot compressive stress versus time of the trial. It presents a general comparison of the mortars when they were subjected to an ECE with respect to those which had no treatment. In all cases the slope was the same (2.085) with a correlation factor of 99.98%, therefore the elastic modulus are equal, having compressive strength not very different.

(Figure 8 here)

4. Conclusions

According to the data obtained we cannot asseverate that the ECE has a negative effect on the compression properties in mortars, instead the results shows that the compressive mechanical behavior is very similar to those specimens that were not treated. Therefore, this technique can be used to extract aggressive ions (such as chlorides) in a short period of time, without reducing their mechanical properties in compression. Although a slight modification was found in the microstructure of the transverse sections of the steel rods after applying this method (6 A/m^{2}and 9 A/m^2); the technique is able to place the corrosion potential of steel rods in an uncertain zone of probability of corrosion, and if we wait to stabilize the system after a while, it is possible to have a passive steel again, such as some researchers have claimed 2029

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Table 1. Mortar specimens that have been previously contaminated with NaCl,
shows the current densities used in the experiment
Table 2. Radial thickness in the periphery (white area) of the steel rod, with and without ECE
Table 3. Summary of compressive stress level obtained in the cylinders of mortar

Table 1.

Cylindrical sample	Condition	Steel Rod	Contamination		ECE				CI Profile-	Compressive Strength
			Type	Mode	Current density			Time (days)		
			5% wt.NaCl	immersion after a 90-day setting	3 A/m^2	6 A/m^2	9 A/m^2	15		
0		Without rod	Reference only for compression test							
1	NO ECE	1	X	X	Rod embedded in the mortar cylinder. Cylinders used to measure the compressive strength and electrochemical measurements on the steel rods					
2	NO ECE	2	X	X						
3	NO ECE	3	X	X						
4	ECE	4	X	X	1 A/m^2			X	X	X
5	ECE	5	X	X	X			X	X	X
6	ECE	6	X	X	X			X	X	X
7	ECE	7	X	X		X		X	X	X
8	ECE	8	X	X		X		X	X	X
9	ECE	9	X	X			X	X	X	X
10	ECE	10	X	X			X	X	X	X

Table 2.

Type of rod	No. of measurements	Average thickness (µm)
NO ECE	48	41
ECE	144	72

Table 3.

Cure Time	Specimen	Current Density(A/m^2)	Duration of the EEC(days)	Compression maximum effort (Kg/cm^2)	Average Compression Strength (Kg/cm^2)	Condition
90 days	0	0	0	522	522	Reference
90 days	1	0	0	576	576	without ECE
90 days	2	0	0	611		
90 days	3	0	0	541		
90 days	4	3	15	587	600	with ECE
90 days	5	3	15	599		
90 days	6	6	15	590		
90 days	7	6	15	624		
90 days	8	9	15	579		
90 days	9	9	15	624		

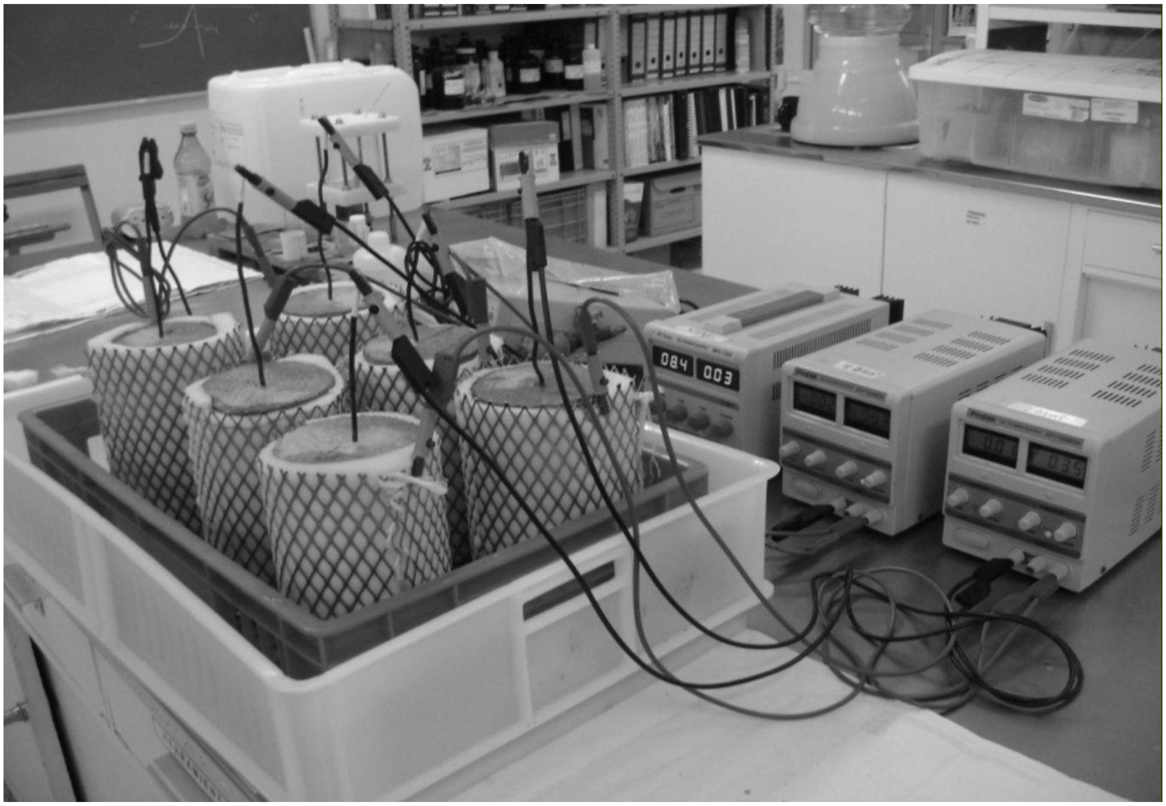


Figure 1

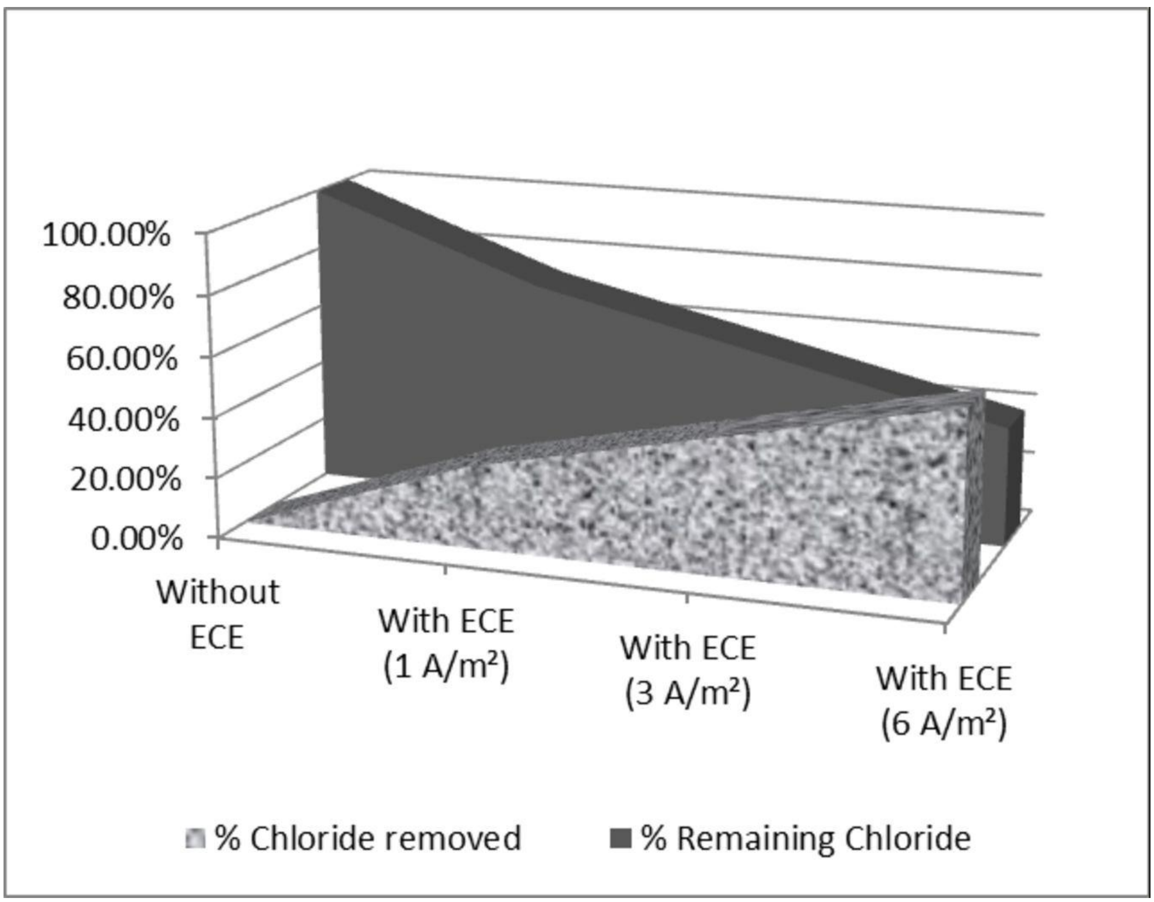


Figure 2

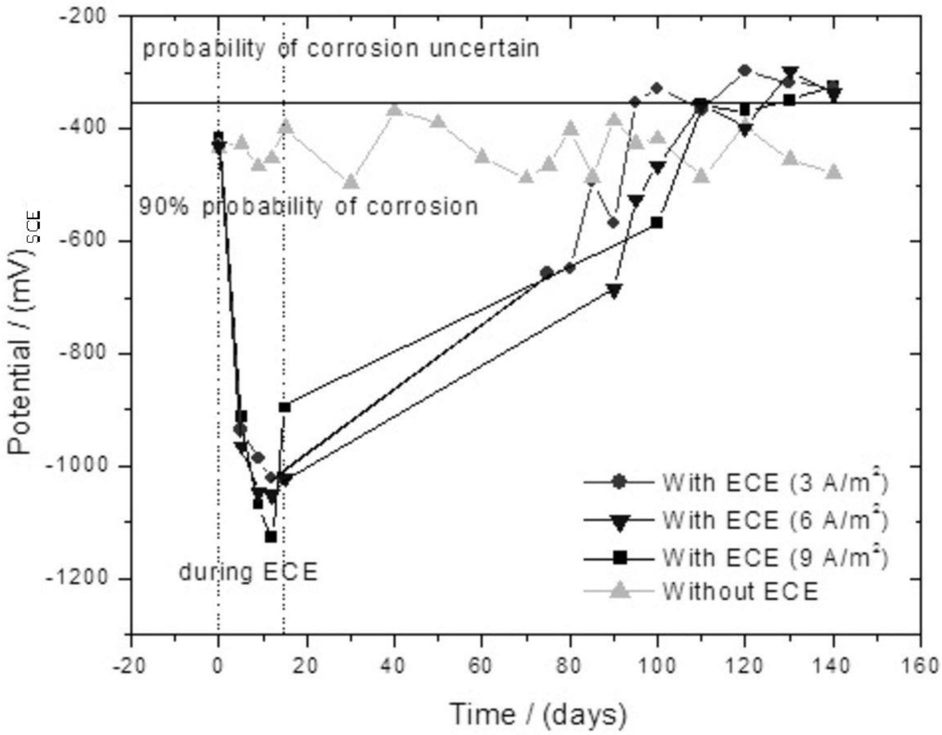
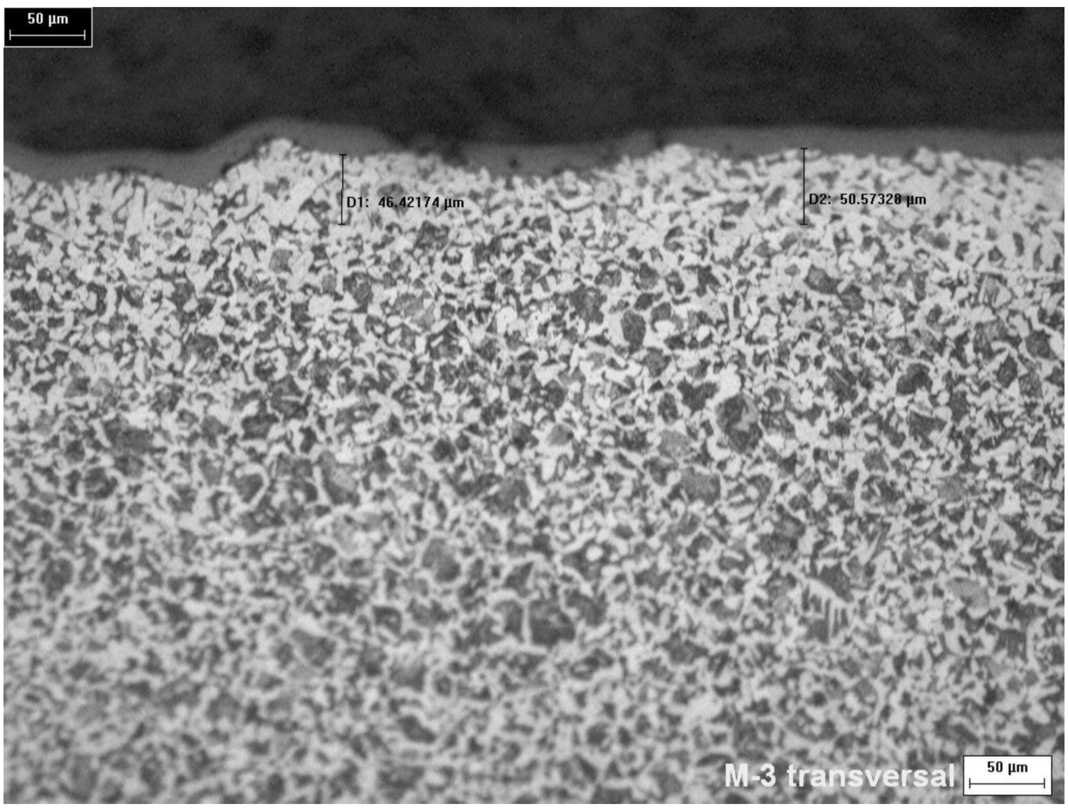


Figure 3



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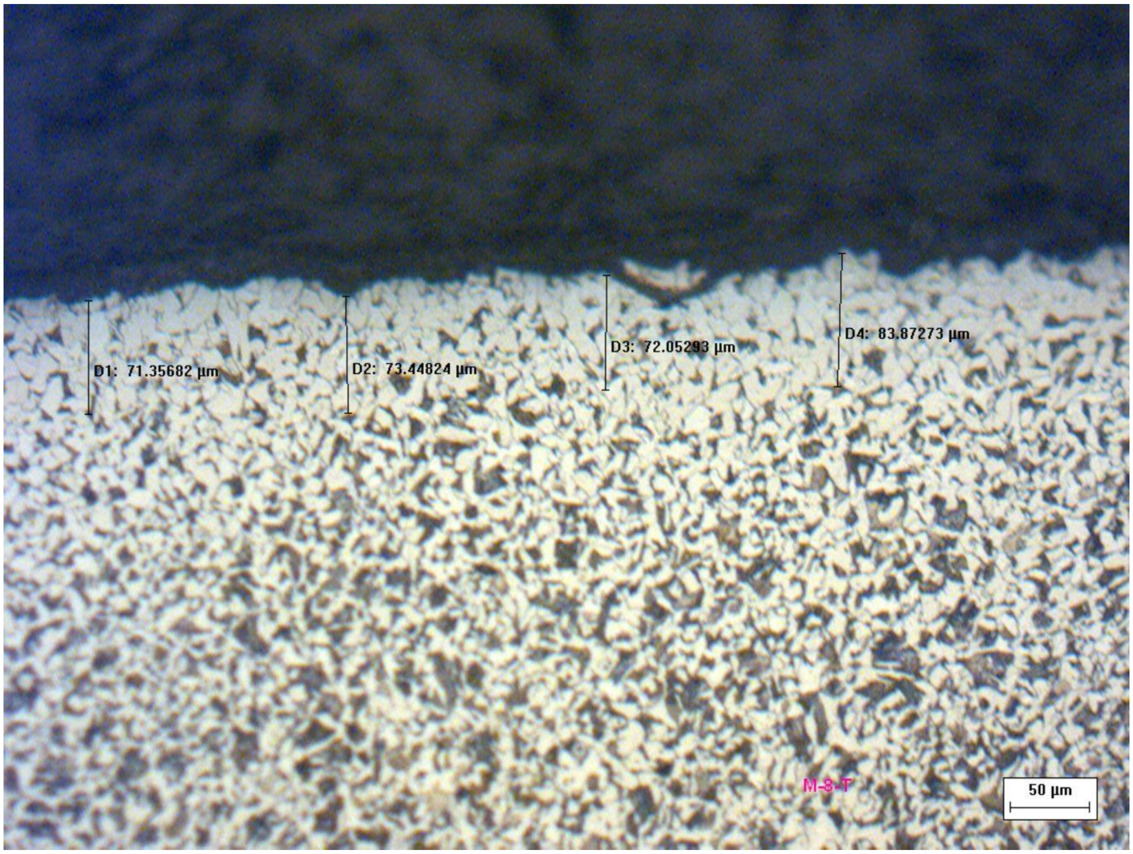

Figure 5

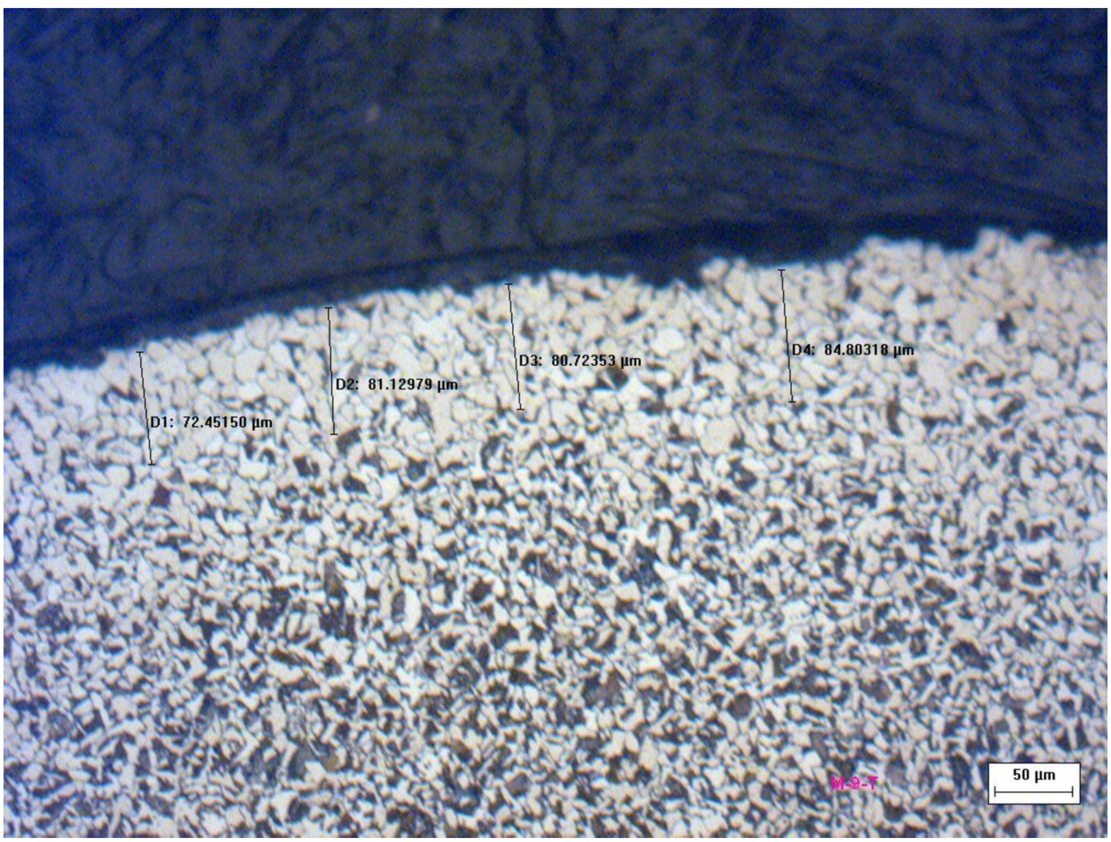

Figure 6

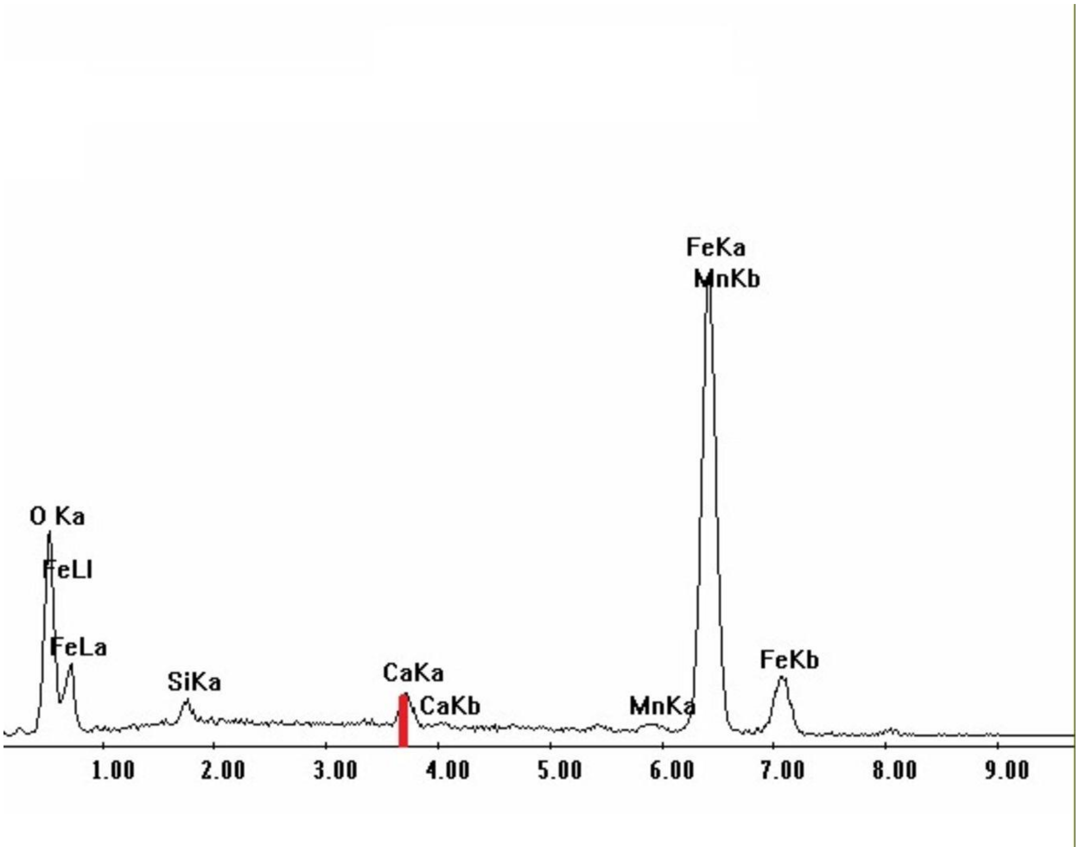

Figure 7

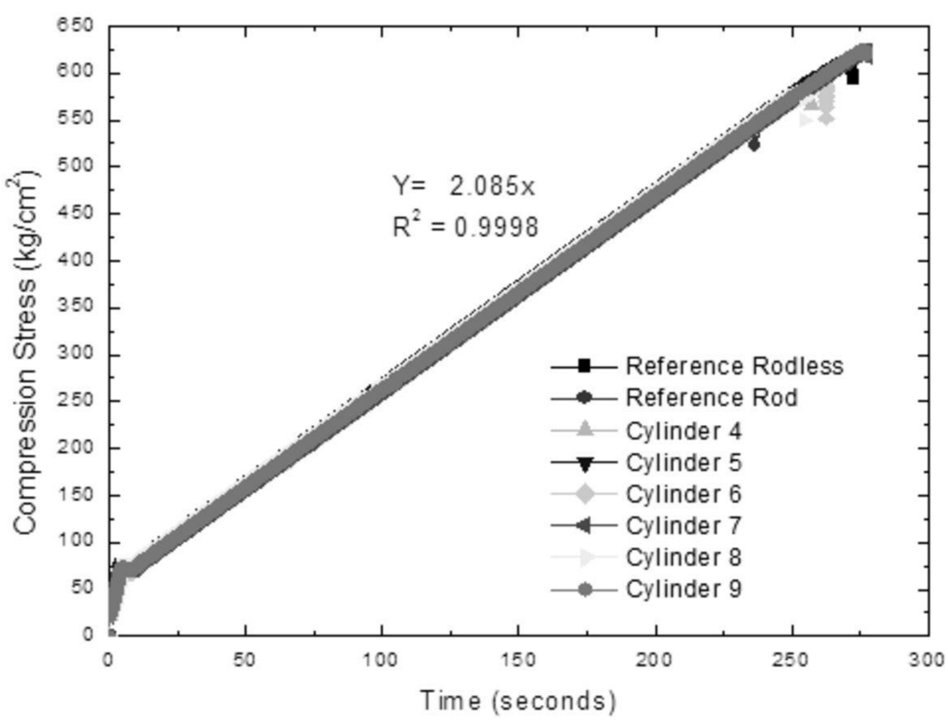

Figure 8