

CORROSION RESISTANCE FOR SOME GALVANIZED STEELS UNDER AN EXTREME ACID RAIN ENVIRONMENT

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Abstract - Hot dip galvanized steels coated with pure zinc films are certified to have high corrosion resistance in atmospheric environments. In addition new galvanized steels, with zinc-aluminum alloy films, have been developed to give materials more anti-corrosive properties and an expected longer service life. On the other hand, our environment is changing rapidly with the progress and growth of human civilization. A serious result of this changing is an acid rain environment. Therefore, we need to know how hot dip galvanized steels, etc. behave in acid environments and how we can protect steel structures from acid corrosion. It is from this perspective that we investigated the corrosion behavior of plated, metal spray, and hot dip galvanized steels under a simulated acid rain environment. The specimens used for these experiments include three kinds of galvanized steels (pure zinc, 5%Al-Zn, 55%Al-Zn film specimens) with and without silicate silicon sealer. These specimens were placed in an environmental aging laboratory to investigate corrosion behavior in a simulated acid rain environment.

Key words: acid rain environment, hot dip galvanizing, aluminum-zinc alloy film, environmental aging laboratory, silicone sealer

1. INTRODUCTION

Our environment is constantly changing. Therefore materials exposed to it need to be modified and updated on a regular basis. Steels used in structural materials are of particular concern. The life of structural materials is of great importance in regards to the economy and safety of global communities. Hot Dip

Galvanizing is applied to structural steels to prolong their service life because they have very high corrosion resistance⁽¹⁾⁽⁴⁾. However, today our environment is changing very rapidly. A key player in this change is acid rain from environmental pollution. In our project, we simulated an acid rain environment by using special apparatus which allowed us to investigate the corrosion behavior of hot dip galvanizing steels. Our experimental setup and results are discussed in this paper.

Hot dip galvanized steels have created and increased the demand for huge structures such as bridges and buildings and landscape materials like electric poles because of their resistance to corrosion under atmospheric conditions. Hot dip galvanized steels coated with pure zinc films are certified to have high corrosion resistance in atmospheric environments. In addition, new galvanized steels, with zinc-aluminum alloy films, have been developed to give materials more anti-corrosive properties and an expected longer service life. We investigated the corrosion resistance of pure zinc coated steels and of zinc-aluminum alloy coated steels under an extreme acid environment.

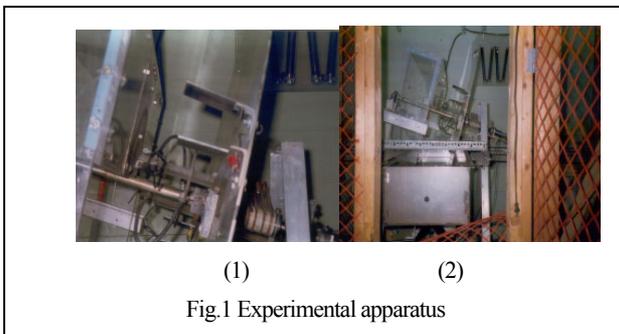
2. EXPERIMENTAL

2.1 Specimens

Three kinds of hot dip galvanizing steels and the substrate were used for this study in the first acid rain test. The substrate was a typical carbon steel (JIS SS400). The specimens included samples coated by pure zinc, 5%aluminum-95%zinc and 55%aluminum-45%zinc films, respectively. The production procedure for the alloy films of zinc and aluminum was a two-step dipping process. First each substrate was dipped into a pure molten zinc bath. Then each sample was dipped into the appropriate alloy bath. For simplicity, the samples used in this project are referred to as 5%, 55%, 100%, and substrate, respectively. In the second acid rain test, some of the samples were coated with an inorganic silicate sealer to confirm the higher corrosion resistance due to surface treatment. For reference, 50%aluminum-50%zinc spray coated steels were used for this investigation and they were compared with those corrosion characteristics of hot dip galvanized steels. A total of 5 samples were tested simultaneously: Galvanized steel by 100% zinc with the sealer, galvanized steel by 5%aluminum-95%zinc with the sealer, galvanized steel by 55%aluminum-45%zinc with the sealer, spray coated steel with the sealer and spray coated steel without sealer. The substrate was also the carbon steel (JIS SS400). For simplicity, the samples used in the second test are referred to as 100P (pure Zn), 55P (55% Al), 5P (5% Al), MS (metal spray without the sealer) and MSS (metal spray with the sealer).

A hole was drilled into all samples. Also corners from all of them were removed and saved for later testing. Next each sample was cleaned with a degreaser, which is a standard for most companies. The degreaser used is called 1,1,2 - Trichlorotrifluoroethane 99%. Then the samples were labeled with permanent ink, weighed, and photographed before undergoing the acid rain simulation test.

2.2 Acid rain simulation corrosion test



For an accelerated corrosion test for acid rain simulation, an environmental aging laboratory was introduced. For the first acid rain simulation test, the samples were tested for 168 consecutive hours using a rotating wheel and a dip tank, which held 92 liters of acid rain solution. (Fig.1) The tank and all components of the setup were made of stainless steel. The samples were attached

to the periphery of the wheel by placing stainless steel bolts through their already existing holes. The substrate

was mounted at Station # 1 of the rotating wheel (just above the red & green wire). The 5% sample was mounted at Station # 2 (just under the substrate). The 55% sample was mounted at Station # 3 (just above the yellow & blue wire). The 100% sample was mounted at Station # 4 just under the 55% sample. The rotating wheel made about 3 revolutions per minute (RPM). Each sample was in the dip tank for half of the cycle and in the air for the other half of the cycle. Sample surfaces were perpendicular to the direction of motion and to the bath. They were dipped flat into the tank's acid rain solution.

For the second acid rain simulation test, the samples were also tested for 168 consecutive hours using a rotating wheel and a dip tank, which held 92 liters of acid rain solution. The same tank and all of its components were again used for this test. The samples were attached to the periphery of the wheel by placing stainless steel bolts through their already existing holes. However, this time the samples attached to the rotating wheel were 5P mounted at the leading outer edge of Station # 1, 55P at the leading inner edge of Station #1, sample 100P at the leading inner edge of Station # 2, sample MS at the trailing outer edge of Station # 2 and sample MSS at the inner trailing edge of Station #2. The rotating wheel made about 3 revolutions per minute (RPM). Each sample was in the dip tank for half of the cycle and in the air for the other half of the cycle. Sample surfaces were perpendicular to the direction of motion and to the bath. They were dipped flat into the tank's acid rain solution.

For both cases, the acid rain solution used in the dip tank had an average pH of 2.6 and an average conductance of 1.2 mille siemens per centimeter (1.2mS/cm). The solution was checked and adjusted daily to maintain these operating conditions. The solution used in this experiment accurately modeled environmental acid rain. It was prepared with sulfuric and hydrochloric acid. Also it contained the following salts: potassium sulfate, ammonium sulfate, magnesium chloride, sodium chloride, sodium nitrate, and calcium nitrate.

Table1 Wetting of specimens for the 1st test

Percent Wetting				
Time	Substrate	Samples		Sample
		5	55	100
1 minute	100% (F)	80% (F)	5% (F)	5% (F)
1 minute	100% (B)	20% (B)	5% (B)	5% (B)
8 minutes	100% (F)	100% (F)	5% (F)	5% (F)
8 minutes	100% (B)	100% (B)	5% (B)	5% (B)
18 minutes	100 % (F)	100% (F)	80% (F)	100% (F)
18 minutes	100% (B)	100% (B)	5% (B)	100% (B)
1140 minutes (1.9 hours)	100% (F)	100% (F)	100% (F)	100% (F)
1140 minutes (1.9 hours)	100% (B)	100% (B)	100% (B)	100% (B)

2.3 Evaluation for the corrosion characteristics

Corrosion characteristics for the specimens were measured in the following four ways: visual examination, gravimetry, wetting and SEM-EDX observations. For the visual inspection, the specimens were observed throughout the tests. The specimens were photographed by a digital camera before and after the tests. For the gravimetry, a 5300 D Fisher Scientific digital Balance was used and the weight before and after the tests were measured for all specimens. Wetting was also measured (by the naked eye) for all specimens intermittently during the tests. After all of these measurements were obtained, the samples were then cut into tiny plates by a cutting machine and served for SEM-EDX analysis. SEM-EDX analysis consisted of cross-section observations by SEM (S-4300 made by Hitachi Ltd.) and element analysis by EDX (EMAX-7000 made by Horiba Ltd.). The acceleration voltage of the electron beam

was 20kV.

3. RESULTS AND DISCUSSION

3.1 First Acid Rain Simulation Corrosion Test

The experiment began on January 29, 2003 at 11:30 A.M. (U.S. time). The pH and conductance

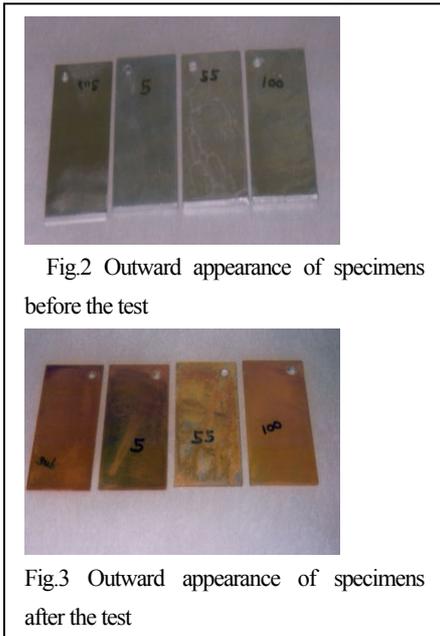
Table 2 Weight change of specimens for the 1st test

<u>Mass Chart (to nearest hundredth</u>					
<u>gram)</u>					
Sample	Mass before testing in grams	Mass after testing in grams	% loss, nearest tenth %)	Change in mass in grams	
substrate	59.81	58.01	3.0	1.80	
100	93.56	91.42	2.3	2.14	
55	87.44	86.12	1.5	1.32	
5	88.01	86.09	2.2	1.92	

measurements at the start of the experiment were (pH = 2.7) and (conductance = 1.22 mS/cm). The temperature in the laboratory was 21 degrees C. The experiment was carried out at room temperature We estimated the percent of surface wetting for the samples intermittently during the test. Keep in mind that the front leading side refers to the front of the sample (the first part of the sample to enter the acid rain solution in the dip tank). The back trailing side refers to the back side of the sample (the side that enters the solution last). The percent wetting for all specimens is shown in Table 1. (Note

that F in the Table represents the front of the sample, while B represents the back of the sample.) The substrate appeared to wet easily. On the other hand, the specimens referred to as 100% and 55% were hard to be wet. The 5% specimen was moderate in regards to the wetting characteristics. Generally speaking, the galvanized steel surfaces were hard to wet. However in any case, all specimens were completely wet after 1.9 hours of testing. The difference of wetting among specimens may be attributed to that of corrosion characteristics or caused by it.

After 8 minutes of testing, the substrate had a yellow color on its surface. After 2.99 hours, the wet



substrate had an orange / brown appearance and the 5% sample looked grey. After 119.2 hours all of the samples had rust throughout the entire surface except for the 55% sample. This sample had about one-third of its surface covered with rust. The substrate had an orange rust and the 5% sample looked like a black / rust combination. The 100% sample had a uniform orange / gray rust and the 55% sample appeared gray with about 30% of its surface a yellow / orange color. At the end of the experiment (after 168 hours of testing) when the samples were still wet, the substrate had a uniform orange / rust color. The 5% sample had a uniform black / rust color and the 100% sample had a uniform gray / rust color. The 55% sample had about 60% of its surface covered with orange patches. It should be noted that areas where the samples were bolted to the rotating wheel have less rust because they were protected from the acid rain solution. The results of macroscopic observations before and after the first acid rain simulation test are shown in Fig.2 and Fig.3. On the

other hand, the weight changes for all specimens before and after the first acid rain simulation test are shown in Table 2. The weight change for specimen 100% was the highest and that for specimen 55% was the lowest. It indicates that both iron and zinc corroded and formed corrosion products on the surfaces in the acid solution. The macroscopic examination shows that the corrosion product of the substrate differed slightly from that of galvanized steel samples. For the former, the corrosion products were composed of red rust (Fe_2O_3). On the other hand, it was composed of red rust and white compounds coming from the corrosion of zinc for the latter. From the perspective of corrosion protection for an iron substrate, the latter was more anti-corrosive, since zinc film played the roll as sacrificial anode for corrosion protection. For the galvanized steel specimens, the weight change decreased in this order: 100%, 5% and 55%. It suggests that the aluminum content in the coating layers increased the corrosion resistance for the galvanized steels. Therefore the alloying of aluminum into the zinc film appears to be an effective way to protect galvanized steels from acid rain corrosion.

3.2 Second Acid Rain Simulation Corrosion Test

This experiment began on April 7, 2003 at 9:41 A.M. (U.S. time). The pH and conductance measurements at the start of the experiment were (pH = 2.6) and (conductance = 1.2 mS/cm). The

Table 3 Weight changes of specimens in the 2nd test

Mass Chart (to nearest hundredth gram)				
Sample	Mass before testing in grams	Mass after testing in grams	% loss, nearest hundredth%)	Change in mass in grams
MS	121.12	119.64	1.22	1.48
100 P	91.75	91.68	0.08	0.07
55 P	88.11	88.09	0.02	0.02
5 P	89.17	88.97	0.22	0.20
MSS	122.05	121.90	0.12	0.15

temperature in the laboratory was 21 degrees C. The experiment was carried out at room temperature. Also in this test, the wetting was estimated intermittently for all specimens. After 30 minutes the MS sample appeared to be 100% wet. After 3.8 hours of testing, the 100P sample appeared to be 100% wet and the MSS sample looked 100% wet after 5 hours of testing. After 6 hours of testing all five samples were 100% wet. In this case, most of the specimens were coated with a silicon sealer. Therefore, the times required for their complete wetting were different from those in the first test.

The samples did not seem to change much in appearance for about several days. At 47.6 hours (of running the experiment) sample 5P displayed black edges with a

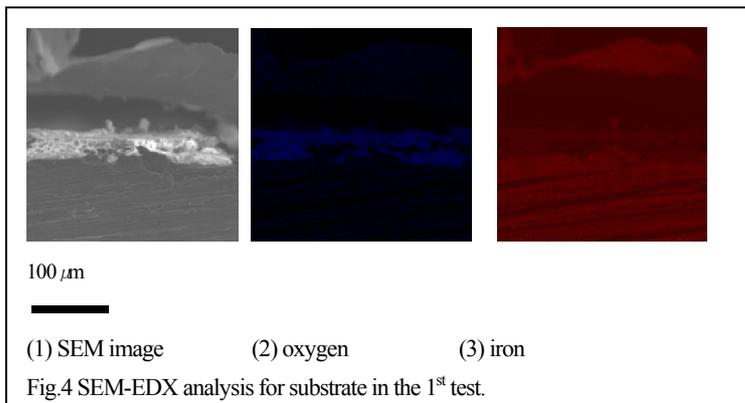
slight gray cast over its surface, sample 55P had some small black spots on the front surface (part to enter the acid bath first), sample 100P had black spots on the back surface, and samples MS & MSS appeared unchanged. At 96.17 hours sample 5P appeared a silver gray color with black edges and black spots on the front surface, sample 55P had some black spots near the edges on the front surface, sample 100P had a few black spots and grains showing on the back surface, sample MS appeared unchanged and sample MSS had a slight yellow color to its front surface. At the end of the experiment (after 168 hours of testing), observations were made of the dry samples. Sample 5P mainly had a light grey uniform surface with small rust lines on the edges. Sample 55P looked silver with gray patches and a few orange/black rust spots. Sample 100P had a light grey layer over silver (for about 80% of the surface) and a few orange rust spots near the edges. Sample MS had a uniform light color (similar to its original color) with minor rust marks near the cut corners. (This rust may be due to rusting of the cut corners. Remember the corners were cut to provide samples for later/additional testing.) The MSS sample had a yellowish surface mainly on the leading face (sample surface which entered the

acid rain bath first). This yellowish surface could be removed easily by wiping and the original color appeared after that. This suggests that the surface of MSS was colored by the solution including some iron oxide which flowed from other parts of the machine. These macroscopic observations indicate that all samples containing a silicon sealer had increased corrosion resistance. This conclusion is confirmed by the gravimetry data. The gravimetry results are shown in Table 3.

For most of the samples in this table, the weight change after the test was very slight. The only exception was MS which did not contain a silicon sealer. Comparing the data in Tables 2 and 3, one notes the drastic decrease of weight changes in the second test for specimens containing a silicon sealer. Even though the weight change of MS was relatively high, it decreased drastically when the silicon sealer was applied (the result for MSS in the same table). The silicon sealer usually penetrates into pores of surface films and sticks fast to substrates. Usually, the spray-coated films have pores in them. Therefore, the sealer can penetrate into the pores and improve the performance for corrosion prevention. Comparing the results for MS and MSS in Table 3, confirms this tendency. However, galvanized steels also show an increase in anti-corrosiveness, when the silicon sealer is applied. The weight changes of galvanized steel specimens in Table 3 were several tenths of those in Table 2. We originally anticipated that the silicon sealer applied to the galvanized steel specimens would not have shown the anti-corrosive performance so much, since it would not have stuck well to their surfaces. However, good anti-corrosiveness was indeed found to exist. It can be attributed to the good adhesion of the silicon sealer to the galvanized steel specimens. The surface of galvanized steel specimens is not as porous as the spray-coated specimens. However, it is pretty concave-convex on a microscopic level. Therefore, the silicon sealer could penetrate into the concave portions to increase the adhesiveness and anti-corrosiveness.

These results suggest that the application of silicon sealer to the galvanized steel can prolong the life cycle of steel structures. Usually steel structures can survive a long time when they are galvanized. The current investigation teaches that 55%Al-Zn plated steels are best for this purpose. However, our study suggests that the application of the silicon sealer can prolong the life cycle even further. Some people may mention the possibility of using other sealers. Most of the other sealers are organic and vulnerable to ultraviolet light. They can decompose in a relatively short time under the exposure of sunlight. On the other hand, the silicon sealer (used in our test) is very stable under such a condition. It can be successfully applied to the steel structures (in our environment) where acid rain and ultraviolet light attack them.

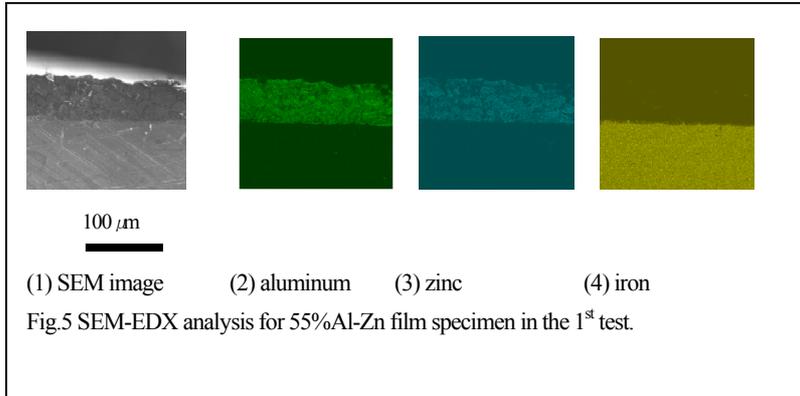
3.3 SEM-EDX Observation



All samples were observed by SEM-EDX after the test. These microscopic observations confirmed the tendencies of the corrosion characteristics for the specimens described above. Fig.4 shows the analysis results for a cross section of the substrate after the test. The SEM photo and the oxygen distribution indicate that thick oxide corrosion products were formed by the simulated acid rain.

On the other hand, Fig.5 shows those results for the 55% specimen. In this case, a sealer was not applied to the specimen. Little oxygen distribution was seen in the surface vicinity. (Therefore, it was omitted from Fig.5.) On the other hand, both zinc and aluminum were found completely in the surface film and the distribution conditions didn't change during the simulated corrosion test. It also

confirmed that specimen 55% was the most stable against the acid rain environment, when no sealer was applied.



When the silicon sealer was applied to the specimens, the SEM-EDX observation confirmed that the sealer penetrated the concave portion of galvanized surfaces and adhered to the specimens to increase their corrosion characteristics.

4. CONCLUSIONS

We investigated the corrosion characteristics of some hot dip galvanized steels with and without an inorganic silicon sealer. The specimens were tested in a simulated acid rain environment using an environmental aging laboratory. The following results were obtained.

- (1) Galvanized steels showed sacrificial corrosion prevention performance for steels.
- (2) The alloying of aluminum into zinc film increased anti-corrosiveness in the environment. For the alloying film specimens, corrosion was prevented by the corrosion products at an early stage and few iron oxides were found on the surface.
- (3) The application of the inorganic silicon sealer to the galvanized steel increased the anti-corrosiveness in the acid rain environment drastically, as well as that of spray-coated steels.

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