FINAL REPORT

The Effects of Acid Fog and Dew on Materials

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Prepared by:

F. Mansfeld
Corrosion and Environmental Effects Laboratory
Dept. of Materials Science & Engineering
University of Southern California
Los Angeles, CA 90089-0241

R. Henry
Environmental Engineering Program
Dept. Civil Engineering
University of Southern California
Los Angeles, CA 90089-0242

R. Vijayakumar
CE Environmental
4765 Calle Quetzal
Camarillo, CA 93010

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Abstract

Field exposure tests have been carried out in order to separate the effects of acidic fog on materials damage from those caused by rain, dew and natural weathering. The test sites were McKittrick and Visalia in the Central Valley and West Casitas Pass in Ventura County. These field tests have been supported by laboratory tests in which materials damage has been determined during exposure to carefully controlled fog water chemistry. The materials tested were galvanized steel, anodized aluminum, flat latex paint (on stainless steel) and high density linear polyethylene. At all three test sites and in the laboratory experiments atmospheric corrosion rate monitors (ACRM) were exposed which give a continuous record of the corrosion rates and the time-of-wetness of the sensor materials.

Analysis of the field exposure results for galvanized steel and the paint samples shows that the corrosivity of the atmosphere at the three test sites must have been very low. This result is confirmed by the ACRM data which show very low corrosion activity. Since corrosion rates were so low approaching those for natural weathering, it was not possible to determine the effects of acidic fog. Based on the aerometric data and the observed corrosion behavior, it is doubtful that acidic fog conditions prevailed for significant times during the exposure period of 1/87 - 3/88 at Visalia and McKittrick. No damage could be determined for the anodized aluminum samples. Corrosion damage to polyethylene could not be detected by simple methods and is therefore not reported here.

The results of the laboratory tests show that exposure to HNO_3 at low pH and to high pollutant concentration increased the corrosion rate of galvanized steel to over 10○m/year. Exposure to HNO_3 caused serious corrosion damage to anodized aluminum and the paint.

1.0 INTRODUCTION

The Kapiloff Acid Deposition Act of 1982 recognized the fact that one of the adverse effects of air pollution is the increased corrosion rate of materials of construction. The California Air Resources Board (ARB) was required to assess the impact of acid deposition and provide information for an assessment of the economic impact of acid deposition on materials. ARB has funded several projects which determine the relationships between acid deposition and materials damage. In one of these projects samples of galvanized steel, nickel, two house paints and concrete have been exposed at three test sites in the Greater Los Angeles area (Burbank, Long Beach and Upland) and at a background site in Salinas, California (1). The exposure tests were started in April 1986 and terminated in March 1988. In a second phase of this project additional samples of aluminum, paint on wood and textile were also exposed (1). In addition to the field tests, laboratory tests were conducted which form the basis for the development of damage functions which express the observed corrosion damage as a function of the environmental species which cause this damage. At all tests sites atmospheric data were collected by ARB. These data were used for the formulation of the damage functions. In addition, atmospheric corrosion rate monitors (ACRM) were exposed which provide continuous records of the time-of-wetness during which corrosion is possible and the corrosion rate during these time periods.

While most atmospheric exposure programs performed so far have investigated the effects of acid rain caused by pollutants such as SO_2, no studies have been performed which specifically address the effects of acidic fog on corrosion. The present project is the first one carried out to determine the degree to which acid fog is involved in determining the total corrosion damage of metallic and non-metallic materials. Fog occurs frequently along the coast of California and in the Central Valley. Recent analyses of

fogwater collected in Southern California revealed significantly higher acidity than for rainwater with the lowest pH measured being 1.7 at Corona del Mar. The fact that catastrophic corrosion damage has not been reported at these locations is probably due to the relative short duration of acidic fog events. The corrosion rate of zinc in HCl of pH = 2.5 is about 5 mm/year.

In this project an attempt was made to separate the effects of acidic fog from those usually measured in exposure tests which include the effects of dew and rain. Rain can have an accelerating effect by providing moisture which makes the corrosion process possible, but can also be beneficial by cleaning the exposed surface from deposited pollutants and corrosion products. In order to determine the effects of acidic fog on corrosion in the present project, the test coupons were exposed in two conditions: uncovered to the environment and also under a roof which prevents exposure to rain and the formation of dew. A comparison of the corrosion rate data for the two exposure conditions will provide information concerning the effects of acidic fog on corrosion. Atmospheric corrosion rate monitors (ACRM) were exposed in the same manner and provided a continuous record of the corrosion behavior of the sensor materials. Three test sites were selected at locations where fog occurs frequently, but rainfall is scarce. These sites were McKittrick and Visalia in the Central Valley, and West Casitas Pass, which is close to the urban areas of Santa Barbara, Ventura County and Los Angeles. The first two sites were selected to study the effects of winter fog, the third sites was selected for a study of coastal summer fog. Exposure tests at McKittrick and Visalia were carried out between January 1987 and March 1988, while exposure at Casitas Pass lasted from June to October 1987. The three test sites were collocated with existing ARB monitoring sites at which air quality data were collected. A fog sampler was installed at each site for collection of fog water samples. However, the device used did not perform satisfactorily and therefore no fog chemistry data

could be determined.

The materials for this study were selected on the basis of their economic significance and their expected corrosion resistance to acidic fog. Galvanized steel, anodized aluminum, vinyl acrylic latex house paint and polyethelene were exposed at the three test sites and in the laboratory tests in which the effects of variation in the fog chemistry were studied under carefully controlled conditions. These data are needed for an assessment of the significance of the corrosion rate data obtained in the field tests. In the laboratory tests fog solutions were made up of H_2SO_4 or HNO_3 with pH values between 2 and 4. In some tests chloride ions were added to the fog solutions. ACRMs were also exposed in the laboratory tests.

2.0 FIELD TESTS

The field experiments consist of exposing selected materials at the three test sites for different time periods and determining the corrosion damage. At each site, all materials are exposed in two fashions: under a roof, but with no sides, (except for short rain curtains), and without a roof. In general, the surface wetness of the uncovered samples and the resulting corrosion damage are affected by fog, dew and rain. Since materials damage occurs mainly during surface wetness and since sites with low rainfall were selected, the selected approach, as a first and general approximation, is expected to separate the fog and dew effects. That is, damage under the roof will be mainly due to fog, while for the uncovered samples it will be due to fog, rain and dew. This argument also assumes that the surface wetness due to moisture adsorption by corrosion products is relatively small. This assumption may be valid only during drier periods. The practice of exposure under a roof to separate the condensation effects on materials damage is common in Eastern Europe.

2.1 Site Selection

To measure the effects of fog and dew on the corrosion behavior of materials in the field, three California sites were used (Fig. 1). As discussed above, rain, fog and dew are three causes of surface wetness, and corrosion damage occurs mainly during surface wetness. Since the main objective of the program was to study the effects of acidic fog on materials, sites where rainfall is scanty and fog is frequent were selected. This approach is expected to improve the ability to measure fog effects without major effects from rain. All sites were collocated with existing CARB air monitoring sites so that air quality data were available without duplicating the monitoring effort.

For this project, two sites were selected in the San Joaquin Valley to investigate the effects of winter fog. McKittrick, at the southwest side of

the valley in a petrochemical production area, was selected for higher acidic fog conditions. Visalia, in the east central region of the valley in an urban and agricultural environment, was selected for the fog chemistry developed in its environment. Climatologically both sites receive scant rainfall.

West Casitas Pass was selected as the third site for its proximity to the coast, occurrence of low stratus cloud fog and proximity to the urban areas of Santa Barbara, Ventura and Los Angeles counties. Rainfall during the summer fog season is essentially zero at this site. This site was selected to investigate the effects of coastal summer fog.

2.2 Materials Selection

For this study, galvanized steel, flat latex paint, anodized aluminum and polyethylene were materials of interest to CARB. Zinc (galvanized steel) and paints are the most important materials in terms of the economic loss due to acid damage. Anodized aluminum and polymeric materials are increasingly used and may have substantial economic losses due to acid damage. According to industry sources, flat latex paint is the most popular variety of paint sold in California. The color selected was an off-white. The paint was applied on stainless steel substrate which was selected to separate paint damage from corrosion of the substrate. For polymer, high density linear polyethylene was used. For galvanized steel, electrogalvanized steel was provided by CARB. A chromate surface treatment is often used to enhance the initial weathering properties and the corrosion resistance of galvanized metals. Elimination of this chromate treatment facilitated damage measurements to zinc during the relatively short exposure periods of this project. The edges of the samples were covered by a protective paint. Atmospheric Corrosion Rate Monitors (ACRMs) with nickel and zinc sensors which measure continuous corrosion rates were deployed at each site and in the laboratory tests. ACRMs with paint coated sensors were also exposed to investigate the degradation of the

protective properties of paints by measuring the corrosion currents under the paint layer.

For anodized aluminum, aluminum 1100 series H-14 was processed by a Type II, Class I sulfuric acid anodizing and hot water sealing for a film thickness of 10 m without color (clear anodization).

2.3 Test Procedure and Corrosion Damage Measurements

A detailed description of the test procedures and the methods for damage measurements appears in Appendix A.

2.3.1 Test Procedure

Field exposure of the four materials was conducted at the three sites shown in Fig. 1. The exposure periods covered two winter fog seasons in the San Joaquin Valley in 1987 and 1988 and one summer fog season at the Southern California coast in 1987.

The exposure protocol at each site was as follows:

1. All materials were exposed both on uncovered racks (for total exposure) and on roofed racks (to eliminate dew and rain). The racks were built to ASTM specifications (G 50) and sloped 30^o with respect to horizontal facing true south. Porcelain insulators were used to hold material specimens on the rack to prevent galvanic corrosion at the mountings. Figures 2 and 3 illustrate the exposure racks and the test samples including the corrosion sensors.
2. Material samples exposed for each exposure period consisted of four (2 for the roofed and 2 for the uncovered racks) 15.2 cm x 10.2 cm (6" x 4") thin gauge galvanized iron and painted stainless steel coupons and 15.2 cm x

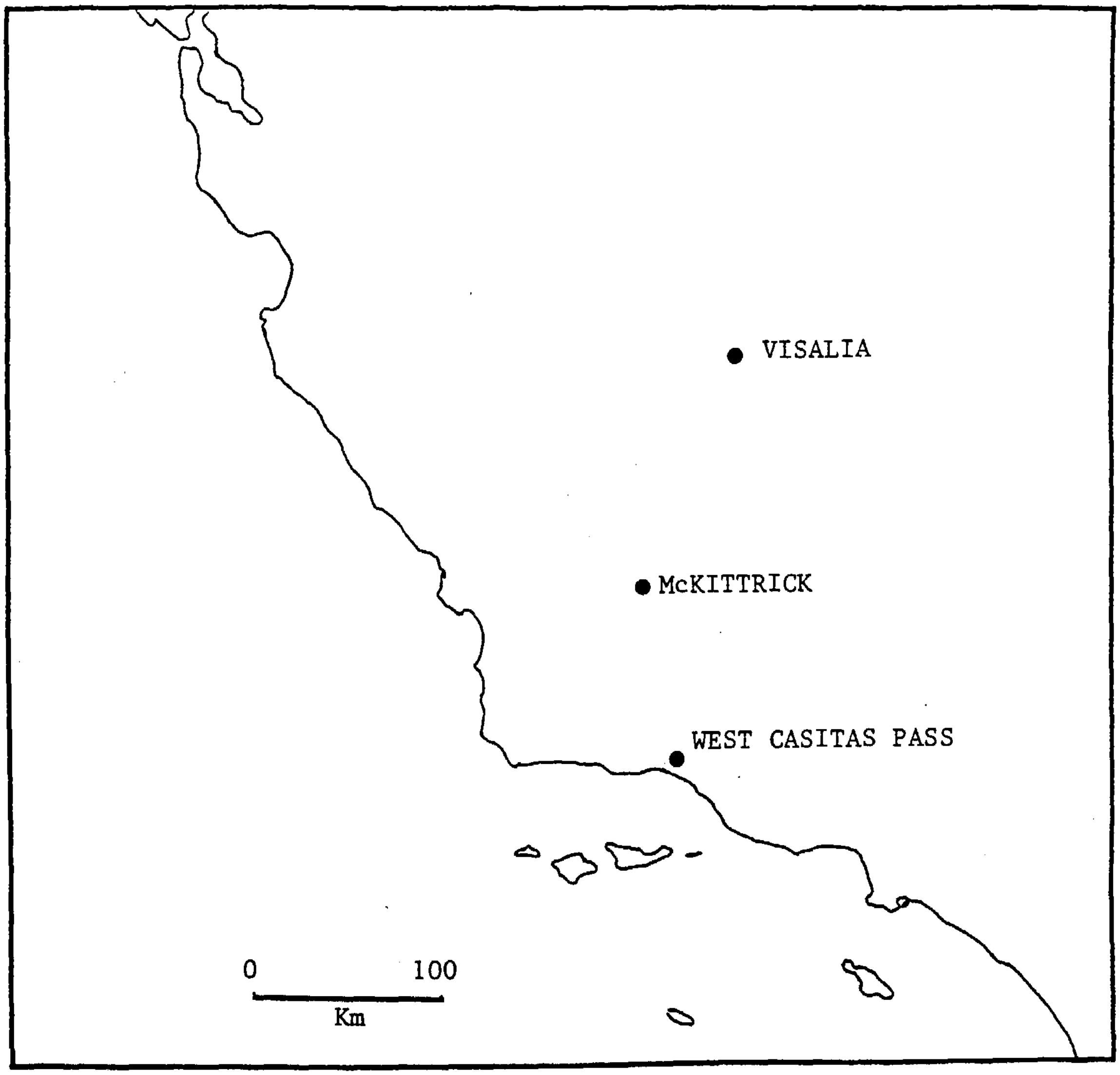

Figure 1 Site location map

Figure 2 Uncovered and covered racks at the West Casitas Pass CARB air monitoring station. Note the rain curtains on the covered rack.

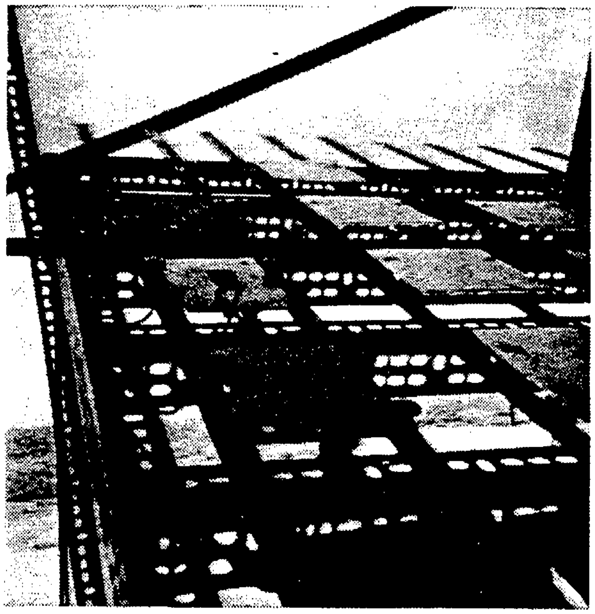

Figure 3 Close up of the corrosion sensors and material specimens under the covered rack at the McKittrick CARB air monitoring station. Note the porcelain insulators holding the specimens.

13.3 cm (6" x 5 1/4") polymeric material coupons. For the San Joaquin Valley test sites there are three exposure periods. One set was exposed for two fog seasons from January 87 to March 88, and two sets were exposed for individual fog seasons, January 87 to June 87 and June 87 to March 88. For exposure to the coastal summer fog at Casitas Pass one set was exposed from June 87 to October 87.

3. Six atmospheric corrosion monitors (ACRMs) (2-4) were exposed at each site for continuous monitoring of instantaneous corrosion rates. Three ACRMs had zinc sensors and three had nickel sensors. The flat latex paint was applied to two of the nickel sensors. One set of ACRMs (zinc, nickel, painted nickel) was exposed uncovered, the other set was exposed under the roof. The ACRM data were collected with the ACRM data logger (ACRMDL) and stored on magnetic tape. The data logger also collected and stored the RH and temperature data (4).

Aerometric Measurement

All field sites were collocated at CARB monitoring stations. The appropriate meterological and air quality data obtained by CARB are utilized in the analysis of the materials damage.

A fog sampler was installed at each site to collect fog water samples which were to be analyzed for NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, and acidity. However, maintenance problems and service time requirements proved to be excessive for this device which was provided by CARB. Among other problems, the wrong types of plastic and glue were used by the manufacturer (Caltech) and the units came unglued after a short period of field exposure. Thus the effort to collect fog water samples was discontinued after collecting only a few contaminated samples. Therefore, no fog chemistry data are available.

Damage Measurement

Quantifying damage by its physical property degradation requires measuring the individual property before and after exposure. The difference in this property is the damage when adjusted for appropriate unexposed blanks. In this project, the physical property used was the weight of the material (to indicate loss of material). Weight loss was used to quantify corrosion damage to galvanized iron and paint. It was determined by exposing pre-weighed samples and weighing the exposed samples after removal of corrosion products by appropriate means. The details of this procedure are described in Appendix A. The weight loss, when corrected for blanks, represents the corrosion damage to the material. From these data corrosion rates can be calculated and expressed as reduction in thickness per unit time (e.g., μm/yr) or weight loss per unit time (e.g., g/m^2 year).

2.3.2 Corrosion Damage Data

The corrosion damage for paint (on stainless steel) and galvanized steel was determined by weight loss. For anodized Al electrochemical impedance spectroscopy (EIS) (5, 6) was used to detect changes on the surface properties as a result of exposure to the atmosphere.

2.3.2.1 Weight Loss Data for Paint and Galvanized Steel

The weight loss data for the three test sites are listed in Table 1 for the paint samples and in Table 2 for the galvanized steel. Data for McKittrick (MK) and Visalia (VI) were obtained for one winter fog season (1/87-6/87, Set #1) and for the combined periods of two winter seasons and the intermedaite summer season (1/87-3/88, Set #2). In addition, weight loss data were also collected for another winter fog season, but exposure was started in the preceeding summer (6/87-3/88, Set #3). The samples exposed in Set #2 cover the same time period as the two separate Sets #1 and 3. For West Casitas Pass (CP) weight loss data were obtained for one summer season only (6/87-10/87).

Table 1

Weight Loss Data for Paint

(Field Exposure)

SITE	SET #	EXPOSURE PERIOD	# DAYS	RACK TYPE	WT. LOSS (MG)	VARIATION	CORR. RATE (mg/day)	REMARKS
W. Casitas Pass	1	6/24/87-10/15/87	113	C	14.8	0.3	0.13	
W. Casitas Pass	1	6/24/87-10/15/87	113	U	43.7	0.6	0.39	
McKittrick	1	1/12/87-6/5/87	144	C	11.9	2.7	0.08	
McKittrick	1	1/12/87-6/6/87	144	U	57.3	8.3	0.40	
McKittrick	2	1/12/87-3/30/88	443	C	28.7	3.7	0.06	σ, n=6
McKittrick	2	1/12/87-3/30/88	443	U	98.5	13.6	0.22	σ, n=6
McKittrick	3	6/5/87-3/30/88	229	C	25.9	0.9	0.11	
McKittrick	3	6/5/87-3/30/88	229	U	52.9	6.3	0.23	
Visalia	1	12/31/86-6/1/87	152	C	9.6	2.5	0.06	
Visalia	1	12/31/86-6/1/87	152	U	54.7	1.1	0.36	
Visalia	2	12/31/86-3/31/88	456	C	18.7	3.8	0.04	σ, n=6
Visalia	2	12/31/86-3/31/88	456	U	86.7	4.6	0.19	σ, n=6
Visalia	3	6/1/87-3/31/88	304	C	19.9	0.4	0.065	
Visalia	3	6/1/87-3/31/88	304	U	55.0	0.9	0.18	

Note: C = covered
U = uncovered
σ = standard deviation
n = number samples exposed

Table 2

Weight Loss for Galvanized Steel

(Field Exposure)

SITE	SET #	EXPOSURE PERIOD	# DAYS	RACK TYPE	WT. LOSS (MG)	VARIATION	CORR. RATE* (mg/day)	REMARKS
W. Casitas Pass	1	6/24/87-10/15/87	113	C	14.5	5.4	0.13	
W. Casitas Pass	1	6/24/87-10/15/87	113	U	17.9	8.8	0.16	
McKittrick	1	1/12/87-6/5/87	144	C	4.3		0.03	1 sample
McKittrick	1	1/12/87-6/6/87	144	U	16.0	0.6	0.11	
McKittrick	2	1/12/87-3/30/88	443	C	22.1	2.7	0.05	σ, n=6
McKittrick	2	1/12/87-3/30/88	443	U	21.3	4.7	0.045	σ, n=5
McKittrick	3	6/5/87-3/30/88	229	C	16.9	2.2	0.07	
McKittrick	3	6/5/87-3/30/88	229	U	5.3	1.7	0.02	
Visalia	1	12/31/86-6/1/87	152	C	-19.0	9.8	----	
Visalia	1	12/31/86-6/1/87	152	U	-20.4		----	1 sample
Visalia	2	12/31/86-3/31/88	456	C	-7.5	2.1	----	σ, n=6
Visalia	2	12/31/86-3/31/88	456	U	1.3	1.4	0.003	σ, n=6
Visalia	3	6/1/87-3/31/88	304	C	-9.7	0.7	----	
Visalia	3	6/1/87-3/31/88	304	U	-9.6	1.4	----	

Note: C = covered
U = uncovered
σ = standard deviation
n = number samples
negative values correspond to weight gain after descaling

*0.1 mg/day corresponds to 0.16 μm/year