EXECUTIVE SUMMARY

INVESTIGATION OF THE EFFECTS OF ACID DEPOSITION ON MATERIALS

Contract Nos. A4-110-32 and A5-137-32

Prepared for
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The Kapiloff Acid Deposition Act of 1982 (California Health and Safety Code, Section 39010.5, 39010.6, 39900 et seq.) requires the California Air Resources Board (CARB) to assess the economic impact of acid deposition upon materials as part of a comprehensive research program to determine the nature, extent and potential effects of acid deposition in California. To accomplish this, the relationship between acid deposition and material damage must be determined. Field exposure and laboratory chamber experiments to quantify these relationships were funded by CARB (contracts A4-110-32 and A5-137-32) and have been conducted in joint projects between Combustion Engineering's Environmental Monitoring and Services, Inc. (EMSI), Rockwell International Science Center (RISC), and the University of Southern California (USC). The investigations began in 1986 and concluded in 1988.

The objectives of this study of acid deposition damage to materials were:

- To determine the damage rate of a number of materials of economic importance in Southern California as a function of acid deposition constituents;

- To determine the contribution of natural weathering to the overall damage rate of these materials, and

- To determine the synergistic, antagonistic, and additive effects of multiple pollutants, as found in the ambient atmosphere, on materials damage, and express these effects as damage functions that correlate damage and pollutant levels.

These three objectives were met through analysis of damage measurement data obtained from exposure of selected materials at four
field sites and in laboratory chamber experiments.

Field measurements were made at three sites in Southern California (Upland, Burbank, and Long Beach) and at Salinas in Central California. Attention was focused primarily on Southern California since it is the area where damage due to acid deposition is considered to be highest due to elevated pollution levels and large quantities of exposed materials. The three Southern California locations were selected to differentiate the effects of different acidic pollutants on materials, primarily nitric oxides, nitric acid, and sulfur compounds. Salinas is a clean location relative to polluted Southern California, and measurements at this site are assumed to correspond to natural or background damage.

The field measurements were supported by experiments in the laboratory where the damage effects of acidic pollutants such as nitric oxides, sulfur dioxide, nitric and sulfuric acid aerosols as well as ozone were determined.

The materials investigated in this program were galvanized steel, nickel, latex paints, aluminum, nylon, polyethylene, and concrete. The choice of these materials was based primarily on the economic losses for damage to materials susceptible to acid deposition attack, and reflects current California usage. In the real world, only a few materials account for the major costs of damage. The economics of materials damage are affected by several factors:

1. Susceptibility to damage;
2. Extent of usage;
3. In-situ cost of products (including material, manufacturing, and placement costs); and
4. Maintenance, repair and replacement costs.

For example, zinc is relatively inexpensive, but because of its widespread use for galvanizing steel, the economic loss due to damaged zinc can be significant. Similarly, the material cost of paint or
concrete is small, but their use is widespread, and in-situ and replacement costs are high because of large labor expense. Hence, their damage is also economically significant.

The quantitative relationships between damage and pollutants are generally noted as "damage functions". On the basis of data gathered during the program reported here, damage functions were derived for galvanized steel, nickel and high carbonate extender paint. Damage to paint, being a coating, was investigated by measurements on painted stainless steel and painted wood samples. For the other materials, adequate damage functions could not be obtained because of insufficient data. It should be noted that these materials were added to the investigations midway into the program reducing the number of available data points.

These damage functions are important in models used for assessing the economic damage to materials. Continued data gathering is recommended to obtained damage functions for all the above materials and reduce the uncertainties in them.

Material damage was quantified by measuring a property of the material (strength, weight, etc.) before and after exposure and taking the difference between the two as the damage. In this study, the corrosion damage for galvanized steel, nickel, aluminum, paint on stainless steel, and concrete damage was determined by weight loss. (Weight loss is indicative of the erosion of material due to interaction with the acidic pollutants.) Damage to nylon was determined by the loss of fiber breaking strength. Damage to paint on wood and polyethylene was also quantified by surface property measurements, but these measurements did not yield meaningful results.

The results from the field tests in Southern California are quite different from those which have been reported in other parts of the world where corrosion rates are greatest during the winter months when relative humidity (RH) and pollutant concentration are highest. In
this study, corrosion rates as determined by weight loss for galvanized steel, nickel, aluminum, latex house paint containing some carbonate extender and nylon fabric were higher in the summer than in the winter. This is illustrated in Fig. 1 which shows the weight loss as a function of exposure time for galvanized steel at the four test sites for the first set of samples which were exposed in March 1986. At the three sites in Southern California corrosion rates became very low between October 1986 and January 1987. This effect was not observed at the Salinas background site where corrosion rates were almost constant for the whole period. Similar results have been found for nickel, aluminum, the house paint containing some carbonate extender and the nylon fabric. It is interesting to note that the loss of breaking strength for nylon (Fig. 2) has a similar seasonal variation as the weight loss for galvanized steel (Fig. 1). The much lower damage at Salinas suggests that the pollutants at the Southern California sites have a prominent effect in determining damage to nylon.

The corrosion rates of galvanized steel, which is considered as one of the four "standard materials" for atmospheric corrosion testing by the International Standards Organization (ISO), were very low at all four California test sites (Fig. 1). These corrosion rates were less than 2 μm/year, a value usually considered typical for clean, rural areas. These low corrosion rates can be rationalized since zinc and galvanized steel in outdoor exposure are attacked mainly by SO₂, which occurs only in very low concentrations at the four test sites. These results also suggest that the other pollutants present and the reaction products of photochemical reactions do not have a major effect on the corrosion rate of galvanized steel.

In both the field tests and the laboratory tests atmospheric corrosion rate monitors (ACRM) were exposed; these give a continuous record of the corrosion behavior of the sensor materials, zinc and nickel. The ACRM-data have confirmed the seasonal variations of corrosion rates as shown in Figs. 1 and 2.
The field tests have been supported by laboratory tests in which corrosion damage was determined under carefully controlled conditions using a diurnal cycle. The samples were exposed for 28 days to the individual pollutants, SO\textsubscript{2}, NO\textsubscript{2} or O\textsubscript{3}, and their combinations and to HNO\textsubscript{3} aerosol of two different concentrations and flow rates. The results of a statistical analysis show that galvanized steel and nickel were affected only by SO\textsubscript{2}, while for aluminum, nylon fabric and the two paints a statistically significant effect was observed in the presence of the HNO\textsubscript{3} aerosol.

Damage functions were determined by regression of the corrosion rates against the variables and products of the variables studied. It should be noted that O\textsubscript{3} and NO\textsubscript{2} themselves did not cause damage – as shown in the laboratory tests – but are surrogates for the components of photochemical smog, such as HNO\textsubscript{3} vapor, organic acids and acidic particles, that presumably cause damage. (Principle Component Analysis indicated that the best predictor of corrosion rate was a principal component associated with smog formation.)

Determination of the damage functions was hampered by insufficient RH–data at the Southern California sites and frequent lack of valid RH and aerometric data at the background site Salinas. This latter problem made it impossible to determine a damage function which can be used to estimate corrosion damage at low or zero pollutant levels. The damage functions determined in this project are therefore valid only for estimating seasonal or yearly average corrosion damage and cannot be used for pollutant levels which are lower than those currently found in Southern California.

A summary of these results shows the following:

- The damage rates were typically higher in the Los Angeles Basin than at the background site at Salinas
- The damage rates were quite small and much less than those from other studies in the eastern U.S. and Europe
The damage rates were typically lower in winter than in the summer. This was partially explained by the lower pollution levels observed in winter.

From laboratory measurements, damage, especially to metals, was primarily dependent on sulfur dioxide being present.
FIGURE 1. WEIGHT LOSS VS. TIME FOR GALVANIZED STEEL, FIRST SET
NYLON FABRIC - FIRST SET

FIGURE 2. REDUCTION IN BREAKING STRENGTH FOR NYLON FABRIC VS. TIME, FIRST SET.