SMOKE AND CORROSIVE INDUSTRIAL REFUSE INVESTIGATION
I 75 High Level Bridge over the Rouge River, Detroit
Construction Project B01 of 82194G

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In a memorandum to G. J. McCarthy on March 5, 1962, W. W. McLaughlin named M. H. Janson to collaborate with the Office of Design in an investigation of the smoke and corrosive industrial atmosphere problem in the area of the high level bridge carrying I 75 over the Rouge River in Detroit. L. W. Kelner was selected as the Design representative. The purpose of the investigation was to determine the nature of the smoke and corrosive atmosphere, and to make recommendations concerning materials and protective treatments that might be required for the bridge.

After a meeting with L. W. Kelner on March 28, 1962, the main tasks of the investigation were outlined as follows:

1. Determine the nature of the corrosive atmosphere. The Detroit Smoke Abatement Bureau, The American Agricultural Chemical Company (Agrico products), and other industrial concerns were suggested as possible sources of information.

2. Determine the effect of corrosive atmosphere on bridge construction materials. This was to be done by the Research Laboratory staff.

3. Recommend control measures to eliminate the most harmful atmospheric contaminants.

4. Advise the Design Office of the effects of corrosive agents on bridge materials and suggest materials and protective measures as required.

This report, which constitutes the fulfillment of Items 3 and 4 in this outline, summarizes the information gained on Items 1 and 2, and contains recommendations for measures to be taken in order to minimize environmental effects on the bridge.

Nature of the Corrosive Atmosphere

The bridge is located in a highly industrialized area in downriver Detroit, where the atmosphere is characteristic of such areas in large cities. While the so-called "industrial atmosphere" is known to be a severely corrosive environment, no unusual problems would have been presented in the present instance if it were not for the close proximity of a fertilizer plant to the structure. This plant, operated by the American Agricultural Chemical Company, has four large stacks and two smaller ones discharging effluents of various kinds in the immediate vicinity of the bridge. Three of these main stacks (one each from the sulfuric acid plant, the power house, and ammoniation plant) are located at distances ranging from 350 to 800 ft from the bridge. The fourth, from the superphosphate plant, is about 75 ft from the fascia of the structure and discharges considerable quantities of gases and particulate matter ordinarily considered very corrosive. The two smaller stacks are from the cooler chamber and ammonia scrubber of the ammoniation plant. They carry some particulate matter and ammonia, but in amounts considered negligible.

The Research Laboratory did not have facilities for quantitative analysis of the effluents from the various stacks, but the American Agricultural Chemical Company engaged George D. Clayton and Associates to make such an analysis. Results of these tests are given in Clayton's report to the company dated July 22, 1963. The Clayton report and additional pertinent data gathered from other sources are summarized briefly as follows:

Wet Mix Stack. The superphosphate plant has a 60-ft brick stack about 75 ft from the bridge fascia. In this plant phosphate rock is converted to gypsum and monocalcium phosphate by the action of sulfuric acid. The rock contains appreciable amounts of fluorides as impurities (mostly calcium fluoride), which are also acted on by sulfuric acid and water in the presence of silicates to form sulfates, hydrofluoric acid (HF), fluosilicic acid (H_2SiF_6), and free silica (SiO_2). Carbon dioxide is also produced from the carbonates in the rock, and traces of sulfur dioxide and hydrogen sulfide from the reaction of sulfuric acid with organic materials in the rock. The effluent is strongly acid. Under normal operating conditions the effluent has a total fluoride content (as HF) of 366 ppm, particulate matter content of 0.46 grains per standard cubic foot, and acidity (as H_2SO_4) of 848 mg per cubic meter.

Dryer. A 150-ft steel stack from the dryer of the ammoniation plant is approximately 350 ft from the bridge. At this plant ingredients for high analysis fertilizers are blended, ammoniated, and dried. Approximately 40 tons of fertilizer are dried per hour to a 1-percent moisture content. This drying process uses 25,000 to 30,000 cfm of air and releases a calculated 4 tons of water per hour, small quantities of fertilizer particles, and some ammonia. A 200- to 300-ft steam plume was observed which trailed off into a light dust cloud after the condensed steam had evaporated. Particulate matter from this stack ranged from 0.30 to 0.35 grains per cubic foot or about 1-1/2 lb per hour. Some ammonia is emitted but the concentration is much lower than in the ammoniator stack. There are two smaller stacks on the ammoniation plant, one for the cooler chamber and the other for the ammoniator. The amounts of particulate matter and ammonia discharged from the cooler stack are negligible, amounting to about 0.004 grains per cubic foot and 200 ppm, respectively. However, the Clayton report indicates quite high concentrations of ammonia from the stack of the continuous ammoniator, the amount ranging from 11,900 to 21,500 ppm. The amount of particulate matter discharged from this stack is small, ranging from 0.025 to 0.070 grains per cubic foot.

Power Plant. Apparently Clayton did not analyze the discharge from the power plant stack, but it was observed when the plant was visited on October 17, 1962. The power plant has a 300-ft brick stack located about 800 ft from the bridge, and discharges coal smoke which usually contains sulfur dioxide, carbon dioxide, carbon monoxide, hydrogen sulfide, moisture, and fly ash. A small smoke plume was visible at the time the plant was inspected.

Sulfuric Acid Plant. An 80-ft lead stack on the sulfuric acid plant is located approximately 750 ft from the bridge. Sulfuric acid is produced by the lead chamber process, which involves the burning of sulfur and uses nitrogen oxides as catalysts. Reaction products consist of sulfur dioxide, nitrogen dioxide, and sulfuric acid. The nitrogen oxides along with small quantities of sulfuric acid account for most of the effluent from this stack. The Clayton report does not mention this stack.

Effects of the Corrosive Atmosphere

There are two principal matters of concern regarding the effects of the corrosive atmosphere: 1) the effect on construction materials in the bridge, and 2) the effect on health and safety of the people traveling over it (as well as possible impairment of driver visibility due to smoke, steam, and dust).

Effects on Construction Materials. It is important to bear in mind that all the various main stacks of the Agrico plant except the one for the wet mix process are at a sufficient distance (350 to 800 ft) from the bridge to allow dilution of these effluents to tolerable concentrations before reaching the structure. These stacks merely contribute to the general corrosiveness of the area's industrial atmosphere. While protection of construction materials (particularly steel) is always a problem in such an environment, there are no unusual factors created by these stacks which would call for special protective measures.

The stack from the superphosphate or wet mix process creates a special problem however, because it would discharge its effluent slightly below the deck at a distance of about 75 ft from the structure. Although this effluent would be extremely corrosive to metals, especially steel, there is evidence to indicate that its effect on concrete would be beneficial rather than adverse.* The hydrofluoric and fluosilicic acids would react with the lime and silicates of the set cement to form calcium fluoride and silica in a manner similar to the action of fluosilicates used as concrete floor hardeners. Concrete treated with SiF_4 is almost completely sulfate resistant, highly resistant to acids, and 40 to 140 percent stronger than untreated concrete.

During an inspection of the Agrico plant in October 1962, it was noted that steel surfaces in the area of the process tanks were heavily rusted, and that both galvanized and painted steel surfaces were showing evidence of attack. Because of the possibility of unusually severe corrosion of structural steel in the vicinity of the wet mix stack, special supplemental specifications have been prepared for this project to require blast cleaning, and an additional, fourth coat of paint.**

From observation in the area of the plant and laboratory tests in a humid atmosphere containing fluosilicic acid, it appears that aluminum and other non-ferrous metals are not seriously attacked. An aluminum storage tank nearby was covered with a uniform, dark-gray, oxide layer, and aluminum storm windows and doors in the neighborhood were somewhat discolored but showed no extensive corrosion.

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* See "Gas Treatment Improves Concrete," Engineering News-Record, April 2, 1964, p. 109, and Discussion of a Report by ACI Committee 201, by Johan Van Der Eerde, ACI Journal, Part 2, June 1963, p. 2075.

** Supplemental Specifications for Blast Cleaning and Painting of Structural Steel (5-12-64).

Pertinent information on construction materials, obtained from the Detroit Edison Company and the U. S. Steel Corporation may be found in the Appendix to this report.

Effects on Health and Safety. The Clayton report goes into considerable detail on the physiological effects of the various pollutants found to be present in the effluents from the Agrico stacks. As mentioned previously, the discharge from three of the four main stacks is far enough away to permit dilution of harmful substances to tolerable concentrations before reaching the bridge. Again, the wet mix stack presents the primary hazard because of its proximity to the structure. The acids from this stack have a very pungent odor and a severe effect on the skin and mucous membranes. According to John T. Hailey, Plant Superintendent, winds carrying stack effluents in the direction of nearby houses have resulted in complaints and subsequent suspension of plant operations until the wind shifted. As a result of these complaints, the Detroit Industrial Hygiene Laboratories analyzed the effluent, but their findings apparently satisfied the Detroit Health Department and no action was taken against Agrico.

It seems certain that the effluent from the wet mix stack could cause serious trouble under certain conditions. The Clayton report summarizes the possible effects from this stack as follows:

> "In summary, the emissions from this stack are highly acid in nature and contain several very toxic substances in high concentration. It is our understanding that this stack is so located that it will be discharging very close to the proposed highway, and at approximately the same elevation. In our experience, this is an extremely dangerous relationship, and one which could result in an immediate hazard to persons using the highway during favorable meteorological conditions, and during periods of traffic tie-ups. The constituents of the discharge are extremely corrosive, which can be expected to damage any metal and glass surfaces exposed to it. It is entirely probable that automobiles parked, for even a short time, would experience glass etching if the discharge from the stack reached them."

Concluding Remarks and Recommendations

From all assembled information, the effect of Agrico stack effluents on public health and safety emerges as the principal and potentially most serious aspect of the problem. Because of the proximity of the wet mix stack, however, and the general corrosiveness of the atmosphere, as well as other harmful contributing factors (winter maintenance practices, for instance), the following recommendations are made for construction materials:

1. Structural Steel. Blast clean and apply extra coat of paint as prescribed in supplemental specifications dated May 12, 1964.

2. Concrete. While no unusually harmful effects on concrete would be expected from the wet mix stack, follow the same construction practices here as on other structures to minimize damage from weather and salt solutions resulting from winter maintenance operations.

3. Bridge Railing. Specify aluminum alloy 6061-T6 for the rails, and aluminum alloy 356-T6 or -T7 for accessory castings. Life of galvanized steel in an industrial atmosphere is approximately 10 years. For aluminum, service life of 20 to 50 years would be expected in an industrial area.

4. Light Standards. Specify aluminum alloy 6063-T6 for the standards and 356-T6 or -T7 for castings. Concrete standards would not be used here, and galvanized or painted steel would be much more susceptible to attack. This recommendation applies also to the police call boxes installed on every sixth light standard.

5. Beam Guard Rail. For galvanized-steel-beam guard rail at the median, specify an extra heavy coating of zinc, preferably 2 oz per sq ft on each side.

6. Sign Supports. Again, specify aluminum alloy 6061-T6.

The discharge from the wet mix stack constitutes a potential hazard to the health, safety, and property of the public. Agrico has not admitted liability and has indicated that the company will attempt to recover from the Department any outlay necessary to control their process within acceptable limits. To facilitate right-of-way acquisition, the Department has decided to subsidize, at least partially, any changes in equipment or operations needed for adequate control of the pollution. To learn the extent of the hazard and find ways of controlling it, the Department retained S. M. Dix and Associates, Inc. of Grand Rapids, Consulting Industrial Engineers, to make a study of the situation last winter. On the basis of their report, submitted in February 1964, the Department is prepared to offer Agrico approximately $36,000 in compensation for the necessary changes. It is expected that negotiations will begin shortly.

APPENDIX

Interviews with the Detroit Edison Company and the United States Steel Corporation

INTERVIEW WITH DETROIT EDISON

M. H. Janson and W. L. Frederick of the Research Laboratory Division met with four members of the Detroit Edison Research Staff in their facility at 6605 W. Jefferson in Detroit on February 21, 1963. Mr. Edward Hines, Director of Research, set up the meeting, which was handled by Mr. Maury Decker. The points discussed are covered successively in the following paragraphs.

Aluminum and Coatings for Aluminum

Detroit Edison built a power plant on Zug Island, a heavy industrial area about 1.5 miles from the Rouge River bridge, in 1957. The exterior of the plant was covered with aluminum siding consisting of type 7072 aluminum cladding over a type 3003 aluminum base. It was emphasized that this aluminum was insulated from supporting steel by Neoprene washers to avoid voltaic action. After 2 years the worst-appearing panel was closely examined. The surface was light grey and covered with pits up to 5-mils deep, which did not go through the cladding. It was expected that these pits would not become deeper and that the surface cladding would continue to weather slowly and protect the base material. This was found to be the case. It was stated that Class C galvanized sheets (1.25 oz zinc per sq ft) would last only 3 to 5 years under the same conditions.

A DuPont vinyl fluoride coating for aluminum known as "Tedlar" is said to be advertised for a 20-year life. Acrylate coatings by Rohm & Haas were also noted as having good durability on aluminum.

Steel and Steel Coatings

Detroit Edison has been building transmission towers of galvanized steel angles, and painting them when the galvanizing deteriorates. The galvanizing has lasted 20 to 30 years in outlying areas, but considerably shorter times in industrial areas. A two-coat paint system based on a "Subalox" lead primer once used to paint these towers has now been replaced by a single 2.5-mil brush coat of a polychloroprene system to effect economy. Their plans now call for building the towers of Cor-Ten steel which will not require painting.

A final cleaning of steel structures with 35-percent isopropyl alcohol just before painting was recommended. Painting within 30 minutes of the final cleaning was considered necessary to prevent the buildup of harmful airborne contaminants.

Detroit Edison has encountered problems with corrosion under the anchor plates used to attach transmission towers to concrete foundations. An effective solution was to seal the steel plate to the concrete with a Thiokol sealer to exclude water. These sealers have lasted over 25 years in similar applications on buildings. Major suppliers of these sealers are 3M and Thiokol Corporation.

A Subalox 508 lead base paint was recommended as a maintenance paint for cyclone fencing when the galvanizing has deteriorated. No information was available on plastic-coated fencing.

Detroit Edison's tests indicate that aluminum-coated steel might be as good as galvanized steel, but is no better. They had just received samples of a new aluminum-alloy-coated steel which was claimed to be far superior to previous materials. These claims agree with the opinion of Seymour Coburn of U. S. Steel who said that aluminum coatings showed great promise.

The Utilities Research Council has found that galvanized Cor-Ten steel gives excellent service when corrosive conditions are severe. This is due to the ability of Cor-Ten to accept a heavier than normal zinc coat and to its natural corrosion resistance. This material is presently used for hardware and small structural parts by utility companies.

Cadmium-plated steel was noted as being quite unsatisfactory for outdoor exposure.

The Detroit Edison people were familiar with a railroad bridge which was previously inspected by Highway respresentatives to gauge the corrosion problem in the area of the proposed bridge. They said this bridge had been condemned 8 years ago and needed extensive steel replacement before it could be reopened.

Concrete

The problem of deteriorating concrete has not been serious for Detroit Edison. As a precautionary measure, they extend the coatings used on steel over the top of the concrete foundation under the steel.

INTERVIEW WITH U. S. STEEL

During the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, W. L. Frederick visited the U. S. Steel Corp. Research Laboratory at nearby Monroeville on March 6. Seymour Coburn had extended an invitation to inspect their test samples, while attending a meeting in Lansing on January 23, 1963, concerning steel for the I 75 high level bridge.

Numerous samples of Cor-Ten steel were exposed in a test plot. All appeared to resist corrosion well without any coating. Some samples which had been returned from exposure periods up to 8 years in industrial areas in other locations were in good condition.

Plain aluminum and anodized aluminum samples were also being tested. Both types weathered well and became dark colored, but the anodized samples appeared to have the lesser accumulation of corrosion products. Anodizing was definitely beneficial.

Aluminum-coated steel weathered much better than galvanized stock at the Monroeville test site. This may reflect the fact that a 1-oz per sq ft aluminum coating is more than twice as thick as a zinc coating of the same weight. Several 8-year old samples were in very good condition. Scratches tend to be self-healing and do not permit corrosion to spread.

The coatings research director at U. S. Steel did not recommend any radical changes from normal coatings used over a red lead primer for structural steel protection. He stressed the point that workmanship in preparing the surface and applying the coatings was very important. Sand or grit blasting were the recommended surface preparations.