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Tuberculation of Tar-coated Cast Iron in Great Lakes Water

by

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Tuberculation of Tar-coated Cast Iron in Great Lakes Water

—Thurston E. Larson, R. V. Skold, and E. Savinelli—

A paper presented on May 8, 1956, at the Diamond Jubilee Conference, St. Louis, Mo., by Thurston E. Larson, Head, Chemistry Subdiv.; R. V. Skold, Research Assoc; and E. Savinelli, Research Assoc; all of the Illinois State Water Survey, Urbana, Ill. This report was prepared for AWWA Committee 2810 D—Effect of Purification Methods on Water Main Carrying Capacities, whose function is to advise, assist, and supplement the study being conducted on this subject by the Illinois State Water Survey. The study described is being supported by Research Grant 64007 (R) from the National Institutes of Health, USPHS, Washington, B.C.

THE original objectives of the study reported here were [1] to gather operating data by field references and observations on water main carrying capacities, methods of treatment of municipal waters, and chemical quality of treated waters at various municipalities where carrying capacity tests have been made, and [2] to investigate by laboratory experiments the effect of "free chlorine" (0.5 mg/l) on the corrosion of steel and cast iron by water.

The first objective was essentially attained, and the second, concerning corrosivity of water to steel, has already been reported (1). In that report, basic concepts on the relations of alkalinity and noncarbonate salts to corrosivity were indicated and, for water of Great Lakes character with a chloride-alkalinity ratio of 0.2-0.3 to 1, free chlorine in concentrations greater than 0.4 ppm was shown to increase the corrosion of steel.

Electrical Measurement

At the present time it can be reported that an electrical method has been developed to measure empirically

the instantaneous corrosion rates of specimens. This has been highly satisfactory for laboratory testing of bare specimens. Briefly, the method consists of applying current to the specimen in micro amounts and measuring its change in potential against a reference electrode. The change in potential per unit of applied current density (E/cd) was found to correlate quite well with weight loss measurements converted to milligrams per square decimeter per day as shown in Fig. 1. It is, in effect, a measure of film resistance on the metal surface.

The method described above was used to establish the data on the effect of pH on corrosion of steel in water of a specific quality. The rates of corrosion were confirmed by total weight loss of the specimens at the end of the test (see Fig. 2). It should be emphasized that this relation is specific only for the type of water and at the velocity indicated.

Subsequent laboratory testing indicated that sodium silicate, in concentrations of 2 and 10 ppm, inhibited corrosion of steel by water containing

2.5 equivalents per million (epm) NaHCO_3 with a chloride-bicarbonate rate of 0.4:1 at pH 7.0 and 8.0 and at a constant velocity of 0.14 fps. If specimens were allowed to corrode in water without silica present, however, the subsequent addition of silica up to 20 ppm failed to reduce the corrosion rate in 22 days of testing. These tests were conducted in the absence of calcium.

By providing increased velocity to the test specimens, a decrease in their susceptibility to corrosion was indicated. High rates of corrosion (100 mdd) occurred in waters containing 125 ppm alkalinity and having chloride-bicarbonate ratios greater than 0.2-0.4 to 1, at velocities of 0.085, 0.14, and 0.34 fps; at a velocity of 0.89 fps, however, corrosion at high rates did not occur in waters with a chloride-bicarbonate ratio of less than 0.6:1. In the range of the velocities employed, therefore, the higher velocities allowed greater chloride-bicarbonate ratios before corrosion would take place at rapid rates.

Cast Iron

The part of the study which concerned cast iron had received only superficial attention prior to June 1955. Since then it has received direct attention and has proved to be a very complex problem.

Machined cast-iron specimens were not found to resist corrosion to any significant degree in any type of water under test. Tests made with unground "as cast" or annealed cast-iron surfaces gave evidence of relatively high resistance to corrosion by water of Great Lakes character. It appears that the natural surface skin of iron oxide formed during the process of manufacture is largely responsible for

the excellent reputation enjoyed by cast iron as resistant to corrosion.

By correspondence and by visits to foundries manufacturing cast-iron pipe, it was learned that the interior of all centrifugally cast pipe is partially ground for the purpose of reducing roughness prior to the application of the coal-tar coating or cement lining. In this step, most pipe interiors have been ground to the extent of 10-50 per cent of the surface.

These facts indicate that tuberculation results from action of a non-inhibited water on holidays, or minute holes, in those portions of the tar coating which cover the ground portions of the interior of the pipe.

It is of more than incidental interest to note that the production of the tar-coated or tar-sealed cement-lined cast-iron pipe at some plants now represents as much as 80 per cent of the total production. Because there are many miles of tar-coated pipe already in service where treatment plants are proposed or being modified, however, it is apparent that the immediate objective of the present study is to investigate the effect of water quality on holidays in tar coatings covering ground surface cast-iron pipe.

Roughness

As mentioned in the last report (1), a number of types of roughness are associated with loss in carrying capacity. The truly tormenting type is that of tuberculation, which can be removed with no visual evidence of metal exposure through the tar coating where corrosion may have occurred. A corollary to this phenomenon is the fact that, at some municipalities, little or no tuberculation has occurred, or did not occur until water treatment was initiated. It may be emphasized that

such experience of "no tuberculation" is reported at some treatment plants where calcium carbonate saturation is not attempted. Laboratory tests, therefore, are now directed toward establishing information on the effect of minor concentrations of corrosives and inhibitors on machined cast iron exposed at minute holes (0.02-0.06

as to coating thickness and hole size. The results are promising.

Preliminary observations indicate that for waters with a pH of 7.2, containing 150 ppm of alkalinity and having chloride-alkalinity ratios of 0.1-1.0 to 1, chlorine or chlorine-ammonia compounds in concentrations of 5 ppm cause evidence of corrosion at a greater

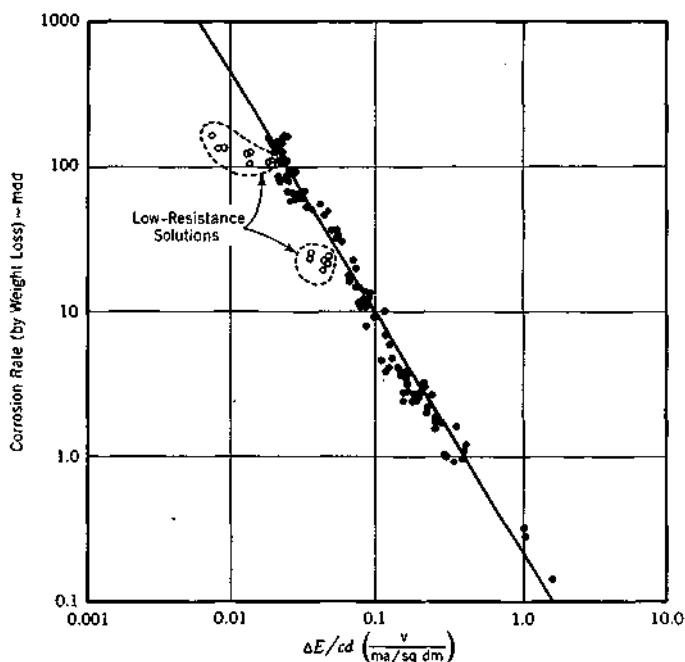


Fig. 1. Empirical Relationship Between Initial Slope of Polarization Curve (Resistance) and Corrosion Rate Determined by Weight Loss

mm) in tar coating. The reason for limiting the exposed area lies in the consideration that minor or nominal concentrations of inhibitors can be considered rather than excessive and abnormal concentrations, as would be necessary for protection of large areas or for uncoated metal.

It has taken months to standardize a technique for duplicating specimens

percentage of pinholes than that observed in the absence of chlorine or chlorine-ammonia under equivalent conditions at pH 7.2. This is still subject to confirmation.

It should be recognized that up to this time no tests have been made with calcium present, as these studies were designed to provide basic data exclusive of the influence of calcium car-

bonate saturation. The literature abounds with information on this principle. There is much data on its effectiveness as well as on its actual or apparent ineffectiveness.

The latest laboratory study on calcium carbonate deposition on cast iron was reported by Werner Stumm (2). Stumm's report is somewhat limited for practical application or confirmation by factors carefully pointed out by the author, and it does not consider the relative basic corrosivity of various water qualities, but it is an important contribution to the literature.

In tests on coated cast-iron specimens with 600 pinholes, with a sodium chloride-bicarbonate ratio of 0.4:1 and a velocity of 0.9 fps, only minor differences in corrosivity were noted at pH 7 and 8. When 0.8 epm calcium replaced sodium in this water, a definite decrease in rate, was observed as pH increased from 7.0 to 7.5 to 8.0, although the saturation index at 8.0 was still — 0.2. The addition of silica or triethylamine in a concentration of 4 ppm had little added influence. It should be recognized that these observations are still to be confirmed by weight loss measurements.

Galvanic Effect

The problem of protecting uncoated machined cast iron is complex in several ways. On machining, the hard adherent skin is removed, exposing flakes of graphite in a matrix of pearlite or ferrite with phosphides. In the laboratory experiments described here, the smallest hole that could be duplicated in an applied tar coating of 0.05 mm thickness was 0.02 mm. The concentration of exposed graphite on the cast-iron surface was such that 85-95 per cent of the holes exposed graphite as well as ferrite or pearlite. This

means that in almost every hole there exists a carbon-iron galvanic cell in which the graphite serving as a cathode accelerates corrosion of the iron. There should be no question but that such a galvanic cell exists, but, for the purpose of providing evidence, carbon rods were coupled with steel specimens, with annealed cast iron and with machined annealed cast iron.

For the steel-carbon couple and the machined cast iron-carbon couple, the potential difference stabilized at 0.5 v after 22 days. For the annealed surface-carbon couple, the potential difference was 0.23 v (this was lower than for the others even though there was one site on the specimen where corrosion occurred at a flaw in the scale or oxide skin). This potential, therefore, actually represents the mixed potential of corroding iron and that of the annealed surface.

Because corrosion by definite galvanic action is present, it would appear that a cathodic inhibitor should be indicated as the corrosion preventive by polarizing or coating the carbon to the protective potential of iron. Calcium carbonate appears to satisfy this criterion for mildly aggressive waters where the area of exposure is at a minimum or where corrosion products are not a detriment. The extent to which silica aids in this process is debatable.

In the analysis of some twenty samples of tubercles and pipe deposits, silica was found to be a significant component, usually consisting of 40-60 per cent of the nonferrous components. This was surprising for Great Lakes waters, because the soluble silica content of plant effluents rarely exceeds 2-3 ppm. Calcium often constituted 15-30 per cent of the nonferrous components, and in about half the samples

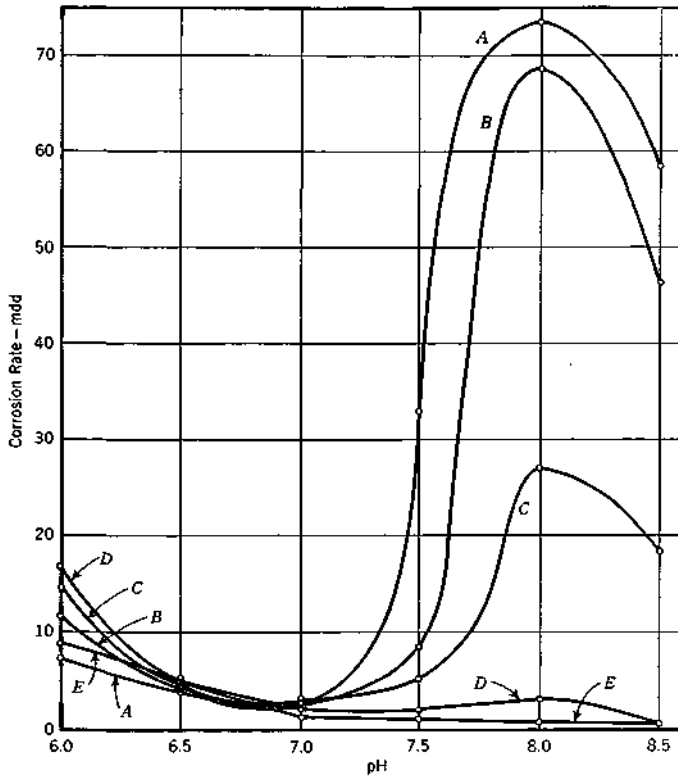


Fig. 2. Effect of pH on Corrosion Rate

The curves indicate results after: A—16 days; B—12 days; C—8 days; D—4 days; and E—2 days. Tests were made on an air-saturated solution with a NaHCO_3 content of 2.5 epm, NaCl content of 0.5 epm, temperature of $19^\circ\text{--}28^\circ\text{C}$, and a velocity of 0.14 fps. This corrosion rate was calculated from AE/cd.

calcium constituted less than 10 per cent. Sodium aluminate or carbonate or both made up the difference. Samples have not been obtained from a sufficient number of municipalities to provide a true evaluation of this approach.

Conclusion

In essence, this report is a summary of specific findings and conclusions. It may be said that this study has become more clearly defined, necessitating a fresh approach to profit further from

the findings made to date. This approach, after months of problems in standardization of techniques, now appears to be bearing fruit. Many negative results have been obtained, but, unfortunately, these are necessary for the elimination of false evaluations.

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