Circular 66

Corrosion and Tuberculation of Cast Iron

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AN evaluation of operation and field data has been made for eleven water plants using Great Lakes water. Laboratory studies indicate the interrelated influences of chloride, alkalinity, pH, calcium, silica, and free and combined chlorine on the corrosion of steel and cast iron by water. Free chlorine was found to be corrosive to steel in water of Great Lakes quality. The greatest single influence on the corrosion of cast iron was found to be the concentration of calcium. Inconclusive results have been obtained to date on the influence of free and combined chlorine and silica on corrosion of cast iron. Tuberculation, a secondary result, or byproduct, of corrosion, was not observed until experiments were made to determine the influence of calcium and the saturation index. From a study *(1)* of available carrying capacity data, it was concluded:

There is no completely satisfactory criterion for external measurement of the physical condition of the pipe interior. This is not a criticism of flow tests when carefully made to determine carrying capacity, however, but an evaluation to indicate a limitation on the extent to which such tests can be used, even comparatively, to determine a change in pipe roughness, specifically tuberculation.

Specific evaluation of treatment methods, or of the relative quality of treated waters, at the eleven water plants studied was not possible due to multiple treatment changes, lack of consistent treatment, or deficiencies in records, sampling, and analytical procedures.

Laboratory Investigations

An empirical relationship (2) was developed between the rate of corrosion and of polarization (change in potential per unit of applied-current density) with very low applied-current density (measured in milliamperes per square decimeter). This relationship is confirmed on all specimens by weight loss measurements at the end of tests.

This method has proved to be invaluable as a laboratory tool as corrosion rates very often do not reach equilibrium for periods as long as several weeks *(3)* and as it permits the measurement of change in rates after **the** addition of rate-influencing ingredients into the environment.

The laboratory tests are performed with metal specimens totally immersed in solution, saturated with air, at room temperature, with carbon dioxide used for controlling pH. The apparatus provides a constant velocity of the specimen in a vertical circular path *(4)*. Cast-iron specimens are machined and abraded with No. 120 grit paper and degreased prior to use. At

been pointed out that a great difference in susceptibility to corrosion exists between "as cast" or annealed cast-iron and machined specimens. It was found *(3)* concerning water with no calcium:

Unlike in corrosion of steel, machined or ground surface cast-iron specimens were not found to resist corrosion to any significant degree in any type of water under test. Tests made with unground
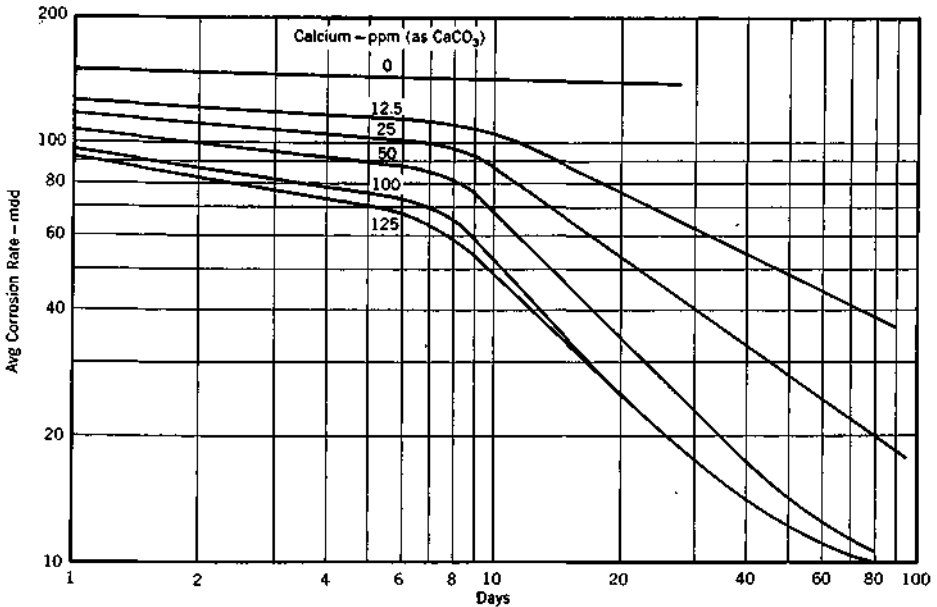

Fig. 1.   Summary of Calcium Effects on Corrosion

Overall averages of test results are shown.   Water velocities ranged from 0.08 to 0.85 fps; alkalinity zvas 125 ppm (as calcium carbonate) ; and tests were run at room temperature.

the end of the tests, the specimens are cleaned electrolytically for 5 min in 10 per cent ammonium citrate prior to the determination of weight loss, in terms of milligrams per square decimeter per day.

Corrosion of Cast Iron

The susceptibility of cast iron to corrosion is unlike that of steel. It has

"as cast" or annealed cast-iron surfaces gave evidence of relatively high resistance to corrosion by water of Great Lakes character in the *absence of calcium..* 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 would indicate that tuberculation results from action of a non-inhibited water on holidays, or minute holes, in those portions of the tar coating
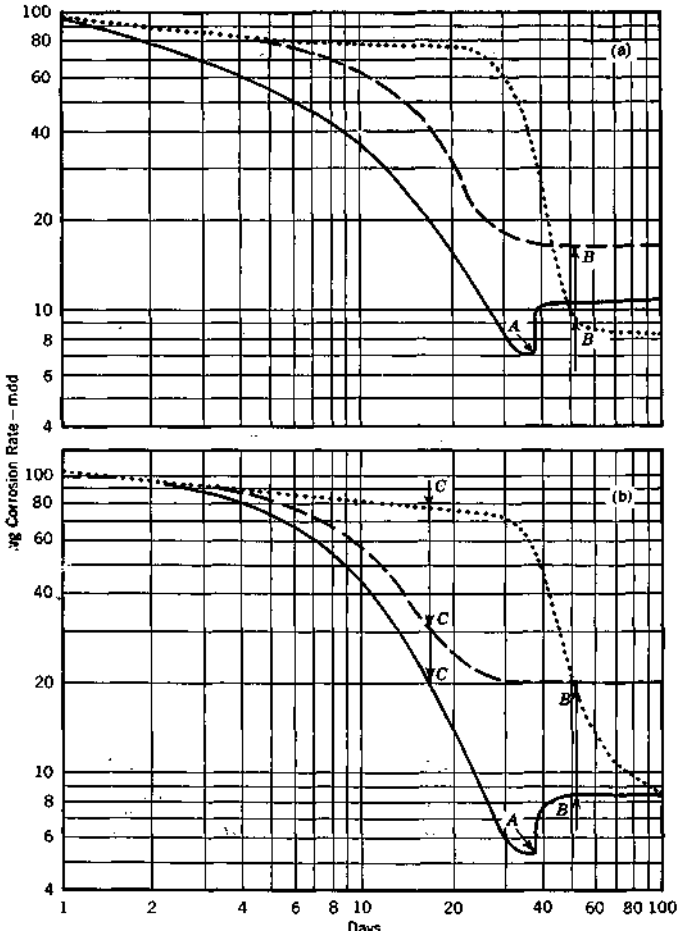

Fig. 2.   Tests Made at 0.085-fps Water Velocity

In both tests, specimens were immersed in 2.5 equivalents per million (epm) of calcium carbonate. The water velocity was 0.085 fps. The dotted lines represent specimens with a saturation index of —0.8 and a pH of 6.8; the dashes, specimens with a saturation index of —0.3 and a pH of 7.3; and the solid lines, specimens with a saturation index of 0.2 and a pH of 7.8 (at Point A, 56 ppm sodium chloride was added, and the saturation index was reduced to —0.1 and the pH to 7.5). At Point B, 0.5 ppm chlorine was added to all three solutions. At Point C, in Fig. 2b, 5.0 ppm silica was added to the three solutions.

which cover the ground portions of the interior of the pipe.

A very considerable amount of effort was devoted to: [1] preparing uniform tar coating on machined specimens and producing artificial holidays of 0.02-0.06-mm diameter for the purpose of simulating the type of coated pipe reported to be in service in many municipalities ; and [2] studying the effect of
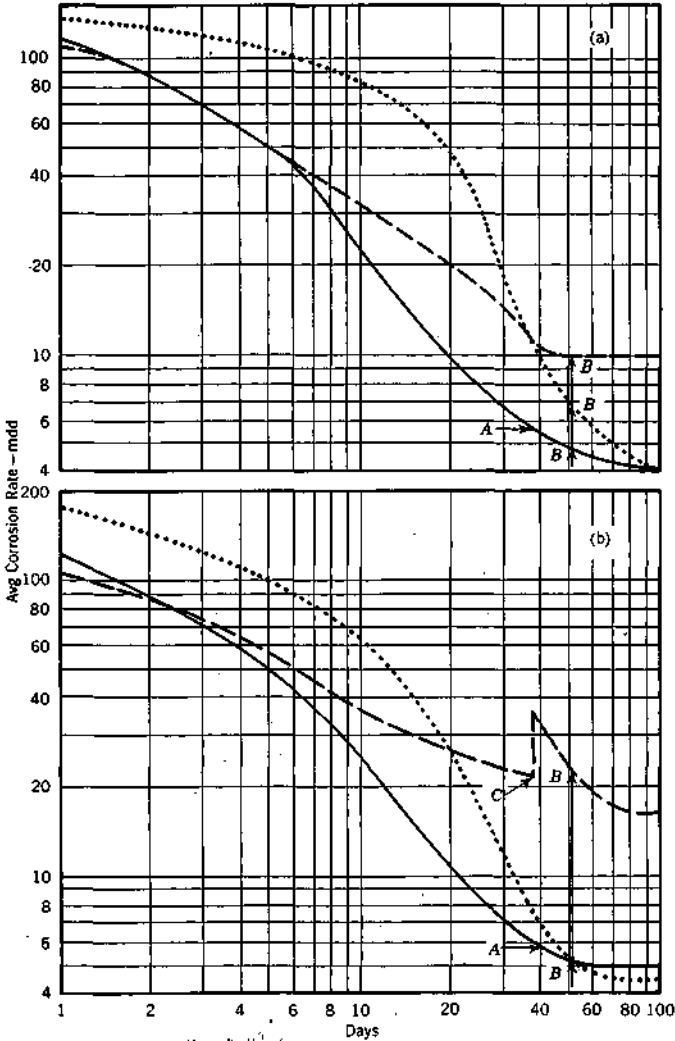
Fig. 3.   Tests Made at 0.34-fps Water Velocity

In both tests, specimens were immersed in a 2.5-epm solution of calcium carbonate. The water velocity was 0.34 fps.   The lines represent the same conditions of saturation index and pH as in Fig. 2, with the saturation index of the third solution lowered to —0.1 at Point A.   At Point B, 1.0 ppm NH₂Cl was added to all three solutions-   At Point C, in Fig. 2b, 56 ppm sodium chloride was added to one of the solutions.

water quality specifically at the holidays. Because the results were inconclusive due to difficulties of reproducing the coating and the apparent porosity of the very thin coating necessary for these tests, this approach was abandoned.

Calcium Effects

With uncoated machined cast-iron specimens in water containing calcium, an interesting overall average of the results is indicated in Fig. 1. This broad generalization indicates that irrespective of the saturation index; of velocities from 0.08 to 0.85 fps; of minor variations in the chloride to alkalinity ratio; and of the presence or absence of chlorine, chloramine, or silica, the concentration of calcium in the presence of alkalinity is a primary factor in the inhibition of corrosion of machined cast iron. It also shows that a certain length of time is required for effectiveness to become apparent.

In this generalization representing all tests, there are broad variations, as much as tenfold in some cases, for each level of calcium. These will be indicated for specific modifications in water quality at the 125-ppm calcium hardness level. These data are represented as smooth lines from the average rates determined five times per week for triplicate specimens.

Figures 2a and 2b show the reduction of corrosion rates with time for three degrees of saturation with respect to calcium carbonate at a low velocity of 0.085 fps. The amount of calcium carbonate was 2.5 equivalents per million (epm). The decrease in rate of corrosion occurred most rapidly for the water with a saturation index of —0.1 and least rapidly for the —0.8-saturation water.

The specimens in — 0.3-saturation water leveled off at a higher final corrosion rate than either of the other two. It should be indicated that these specimens at this saturation index showed small dark reddish spots or growths surrounded by an overall whitish red deposit prior to the addition of chlorine, and continued to form tubercles. Similar growths developed, but to a lesser extent, on the specimens in —0.1-saturation water. The effect of adding 56 ppm sodium chloride is also apparent. (Figure 3 shows that the simultaneous reduction of saturation index was not responsible for this increase in rate.)

The addition of 5 ppm silica at this point had no apparent effect on the corrosion rate, as can be seen in Fig. 2b.

Figures 3a and 3b provide similar data at 0.34 fps, but with combined chlorine present rather than free chlorine. The more rapid reduction and the lower final corrosion rates testify to the effectiveness of a greater velocity to improve the diffusion rate of calcium as the inhibitor. No effect of reducing the saturation index is noted, with this relatively high calcium content.

Similar tubercles, but smaller in size and number, were noted in the —0.3-saturation environment than when free chlorine was present. Parenthetically, the free- and combined-chlorine levels were maintained in these tests without substantial increase in chloride content by periodically withdrawing portions and adjusting the mineral composition with fresh water.

With free chlorine added, it was seen that round knobs of $\frac{3}{16}$-in. diameter protruded as much as $\frac{1}{8}$ in. A clear indication of tuberculation was the pitting evident on cleaned specimens.

Figure 3b shows results almost identical with Fig. 3a and includes clear evidence of the effect of adding 56 ppm sodium chloride to the —0.3-saturation specimen.

One series of tests was made with raw Lake Michigan water transported to Urbana. Single machined cast-iron specimens in each of six modifications in quality corroded in the manner indicated in Fig. 4 and Table 1. The effect of increasing chloride content resulting from chlorine and chlorine-ammonia treatment are indicated to increase the corrosion rate. Tubercles of greater or less magnitude were noted on all specimens, and pitting was also observed.

ratio, and chlorine, the results of four test conditions are indicated in Fig. 5. These specimens showed tuberculation in all cases, with or without chlorine or chloramine, and were similar to the —0.3-saturation index specimens as indicated in Fig. 2 and 3 with 125-ppm calcium hardness.

Although the calcium concentration was lower than in Fig. 2 and 3, the rate of corrosion after 1 day was less than that when 125-ppm calcium hardness was present, since the velocity was greater and the pH higher. Rate of approach to equilibrium is lower.

The influence of the chloride-alkalinity ratio is shown by comparing

TABLE 1

Corrosion and Tuberculation With Lake Michigan Water

Specimen	Treated*	pH	Chlorine	Final $\frac{Cl^-}{Alky.}$	Tubercles	Pits	Final Corr. Rate *mdd*
5	no	8.0	none	0.16	rounded	shallow	25
3	yes	8.0	none	0.16	rounded	shallow	30
4	yes	8.0	NH_2Cl	1.05	small	shallow	49
6	no	8.0	Cl_2	1.05	large	deep	55
2	yes	7.4	Cl_2	1.32	large	slight	73
1	yes	7.4	NH_2Cl	1.50	small	none	90

* Treated with 17 ppm alum and filtered in laboratory.

It should be emphasized that these data are less significant due to the increase in chloride concentration over the 85-day period, resulting from continuous chlorination. Careful analysis of the other variables, however, indicate that fruitful results may be obtained by the careful use of specimens over extended periods of study with the various waters or their modifications in any treatment plant, and by adequate comparison with observations in the distribution system.

To consider further the relative influence of the calcium concentration, saturation index, the chloride-alkalinity

the top and bottom curves; the intermediate ratio of 0.3 is also indicated by the two middle curves. The relative influence of free and combined chlorine appears to be of only minor significance.

Of particular significance is the rise in corrosion rate in one of the solutions at the 84th day, when the pH was permitted to drop to 6.7. On detailed examination of the data, it often appeared that an inadvertent drop in pH of 0.1 unit increased the corrosion rate by about 8 mdd.

Currently, studies have been inaugurated with sulfate, rather than chloride,

to establish the relative influence on the corrosion rate and on tuberculation.

Conclusions

The finding that calcium in the presence of alkalinity, regardless of pH or saturation index, is an effective inhibitor to corrosion is not inconsistent with theory and experience. The basic corrosion reaction is conducive to the formation of calcium carbonate at the

protection is consistent with the well-known action of inhibitors to induce pitting corrosion, rather than general corrosion, when present in insufficient concentration to produce complete protection. This is confirmed by the observation of pitting corrosion on specimens which showed tuberculation. The fact that tubercles form is apparently due to the deposition of a supporting structure of calcium carbonate
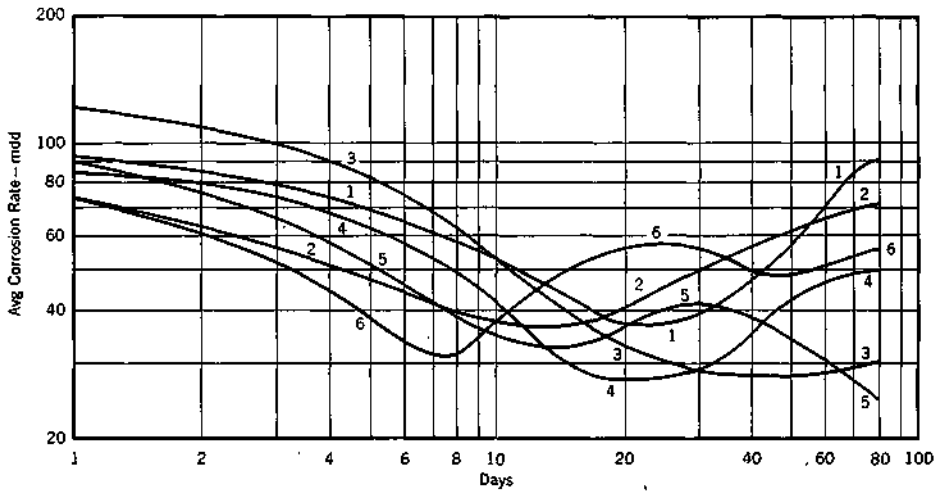

Fig. 4. Tests on Lake Michigan Water

Tests were made on cast-iron specimens, with conditions that varied as indicated in Table 1.

point of corrosion even though the water environment is below saturation with respect to calcium carbonate. The rate at which such deposition may take place is increasingly improved by higher concentrations of calcium or presumably the alkalinity. The rate is also increasingly improved by higher velocities, and is further improved by pH adjustment to or above the saturation pH for calcium carbonate.

The finding that tubercles form under conditions of nearly complete

with or in the normal corrosion product of ferric hydroxide in aerated waters.

If the saturation index is not sufficiently close to zero or the concentration of calcium or alkalinity are too low, the more rigid supporting structure is not developed, although appreciable protection is afforded by calcium carbonate embedded in the rust deposit from generalized corrosion. This was observed on specimens in waters of —0.8-saturation index at pH 6.8 in Fig. 2 and 3. These specimens were

coated with a whitish red deposit of sufficient thickness (about $\frac{1}{16}$ in.) and hardness to continue to adhere even though they were cracked for distances of $\frac{1}{2}$ in. There were no pits under this coating, and it served as an effective barrier to diffusion of oxygen and other corrosive ingredients.

As a tentative conclusion, it appears that the problem of designing water

maintaining or creating a velocity of water flow which is sufficient to provide adequate diffusion, transport, or movement of the inhibitor to the point of effectiveness.

Future Studies

A number of questions remain unanswered. Aside from the need for further data with waters of quality dif-
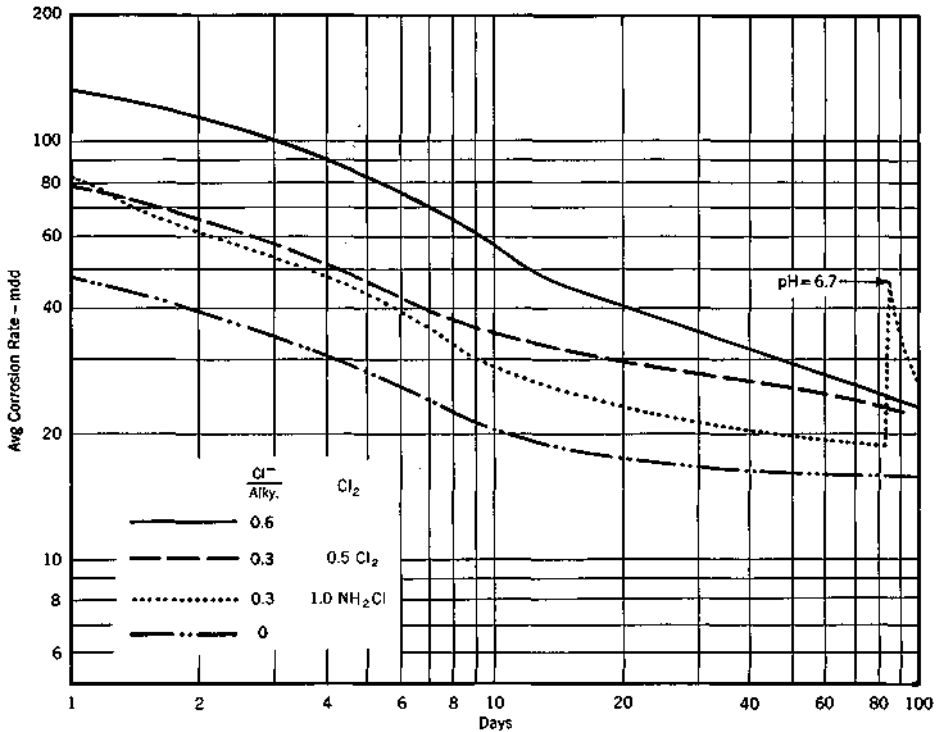

Fig. 5. Effects of Chloride-Alkalinity Ratio

All tests were made with a water velocity of 0.85 fps. Calcium concentration (as CaCO₃) was 31 ppm; alkalinity (as CaCO₃) was 25 ppm. The saturation index was —0.25, and the pH (except as indicated) was 8.0.

treatment to avoid tuberculation of cast iron is limited to such waters as already contain inhibitors in insufficient concentrations to provide complete protection. This problem is jointly concerned with

ferent from Great Lakes water, it will be of interest to establish the relative chemical mechanisms that contribute to the formation and growth of tubercles. Several suggest themselves and are

being investigated to provide a more clear understanding of their interrelationships. More data are required to evaluate other supplementary inhibitors with regard to specific qualities of water.

Study is also required on means of chemically removing existing tubercles without resorting to drastic means and without creating a more corrosive environment.

The data presented here and previously infer that free chlorine can stimulate corrosion and possibly tuberculation under certain conditions. Evidence of this is, as yet, inconclusive. It has been shown that tuberculation can also occur in the presence of combined chlorine and also in the absence of either free or combined chlorine under certain conditions.

It is to the credit of the water works profession that through the years of its history such great interest has been expressed and so much work has been done on the problem of corrosion and occasional associated tuberculation. It is, on the other hand, amazing that so little basic work has been developed by research agencies on this very fertile field of research, although what has been accomplished is significant.

Acknowledgment

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