Corrosion Inhibitors, Coatings and Linings

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INTRODUCTION

Corrosion is a natural, generally unavoidable, harmful process affecting most of the metals, except a few noble ones. Corrosion processes are chemical reactions that take place at the surfaces of the metals. They are undesirable, as they decrease the utility of the metals, either by weakening the section or developing leaks, or by adversely affecting hydraulic carrying capacity.

Nature of Corrosion

In water works terminology, water is said to be corrosive if it attacks any of the metals or materials commonly used in a water works system. Corrosion can also take place externally to water structures such as in pipelines. Corrosion may be divided into three classes on the following lines:—

- (i) Corrosion caused by rapid motion of water (to avoid this corrosion the structure will have to be redesigned to avoid high velocity).
- (ii) Corrosion primarily brought about by the presence of dissimilar metals in a water system.
- (iii) Corrosion caused by the properties of water, e.g., high free CO₂, low pH value, low alkalinity, etc.

There are a number of methods for the prevention of corrosion—one of which being the use of corrosion inhibitors. To understand the action of corrosion inhibitors, knowledge of the principles of electrolytic action is helpful.

THEORY OF ELECTROLYTIC CORROSION AND THE ROLE OF INHIBITORS

If a metal is immersed in a conducting liquid (i.e., water with dissolved solids), certain areas of the metal acquire a different electrode potential from the remainder of the surface, and a positive current flows through the electrolyte from the anodic areas to the cathodic areas, leading to dissolution or corrosion at the anodes. Discussion on corrosion of iron will be more relevant to Water Engineering when one considers corrosion due to (1) differences in the composition of iron at the surface of the materials, (2) differences caused by stress distribution, causing some parts of the surface to act as anodes and other parts to act as cathodes or (3) changes in the quality of water as it flows through the system.

Rate of Corrosion

The difference in potential between the anode and the cathode is the driving force of an electrochemical corrosion process, but the rate of corrosion will be determined by the current flowing round the circuit. Moreover, the anodic dissolution and liberation of electrons must match the cathodic action of consuming electrons at the dynamic equilibrium when no external current is applied.

Let us take a concrete case, where an anodic part forms the half cell with potentialEa, the

cathodic part forms the other half cell with potential Ec. Let the resistances of the paths under the influence of anode be Ra and that under the control of cathode be Rc.

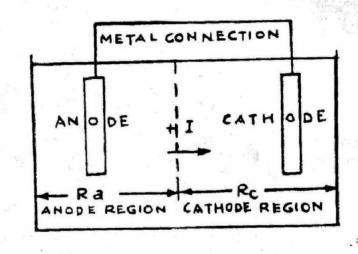
Then, (Ec—Ea) = E will be the driving force for the electrochemical process of corrosion.

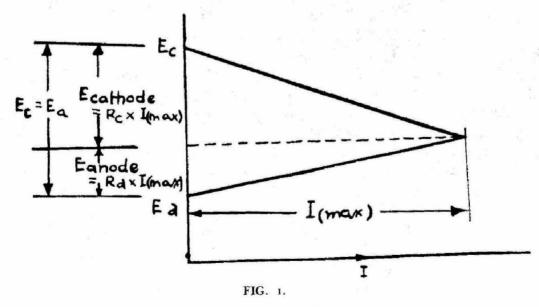
Remembering that at dynamic equilibrium, anodic action of liberation of electrons must match the cathodic action of consumption of electrons; the current 'I' flowing through the anodic region and the cathodic region must be the same in quantum.

In short, total available driving force E shall get so distributed in the anodic region and cathodic region that

and E anodic + E cathodic = E = Ec - Ea.

Diagramatically, this can be represented as in Fig. 1 where the current I is a measure of rate of corrosion.





Electrochemical Process of Corrosion.

Action of Inhibitors

For corrosion to continue, both the anodic action of electron liberation and the cathodic action of electron utilization shall have to continue and the two must match each other. If either the anodic action or the cathodic action is stifled, the corrosion reaction is inhibited.

Anodic inhibitors: Sodium hydroxide, carbonates, silicates, borates, certain phosphates, sodium chromate and nitrite and sodium benzoate are common anodic inhibitors mostly used with iron. All of them, however, are not used in municipal water systems.

The action of anodic inhibitors is to check the anodic action of electron liberation, by increasing the resistance in the anodic path from a value of Ra to (Ra + Rai). This is done by the creation of a coating on the anode. The total driving force (Ec — Ea) will have to be redisbributed in the anodic and cathodic regions in such a way as to have a new value of current common to both. This can only happen with the decrease in the current as shown in fig. 2. The corrosion rate, which is proportional to current, thus gets reduced from Imax. to I as shown in fig. 2.

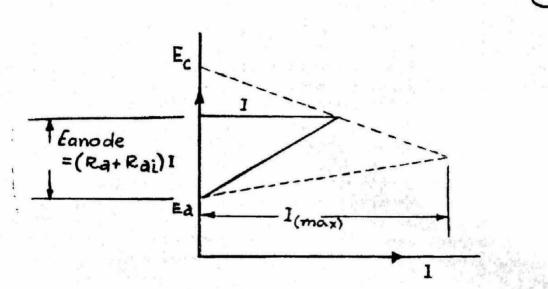
Cathodic inhibitors: Zinc and magnesium sulphates, calcium bicarbonates, etc., that act as cathodic inhibitors, choke the cathodic action of electron consumption or utilization by increasing the resistance in the cathodic path. The increase in the resistance is again by the formation of a coating. Assuming that the resistance in the cathodic region increases from Rc to (Rc + Rci), the current-driving voltage curve gets modified again to give a reduced equilibrium current and so reduced corrosion rate, as in fig. 2.

Inhibitors in Municipal Water Supplies

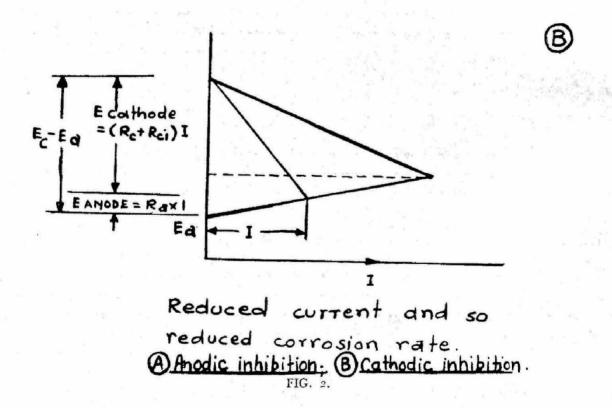
The term 'inhibitor' (from the Latin 'inhibere' to check) or 'corrosion retarder' describes substances which retard, and in some cases almost completely halt the destruction of metals in corrosive media. Inhibitors, used for a long time exclusively in liquid media, are now also used in gaseous media, as well as in the form of solid to semi-solid materials such as paint films, packing materials, coatings and linings.

Inhibitors for acidic corrosion were known as far back as the Middle Ages, when they consisted chiefly of organic substances. About the beginning of the 20th century, inorganic inhibitors, then termed "passivators", were used more commonly. They were added to water and neutral aqueous solutions of electrolytes to retard corrosive processes in these media. Comparatively recently, some organic substances, among them benzoic acid salts, certain amines, and amine nitrites were found to be effective as inhibitors against rusting of steels in water, aqueous salt solutions and antifreezes. A later discovery was that organic inhibitors possessing a sufficiently high vapour pressure can dissolve in the water film, forming on a metal surface in a moist atmosphere, and retard atmospheric corrosion¹.

Municipal water supply authorities have had their share of corrosion problems in their water systems. Although blessed with low temperatures than industrial waters, municipal distribution systems are much more complex, with greater metal surface exposed to water, lower flow rates, and even dead ends or stagnant areas. Moreover, municipalities cannot reuse water, as industries can do, and they suffer more restrictions with respect to toxicity, colours, tastes and odours².



I & I(max) . Reduced current and so reduced corrosion rate.



Perhaps the first attempt at combating corrosion in municipal supply networks was made around 1934 by adding lime or soda ash, to raise pH and to eliminate "red water" complaints. But, it was soon found that the reduction in complaints was due to precipitation of corrosion products as tubercles rather than due to decrease in corrosion rate. Lime was, therefore, added to render the water scale-forming, so that calcium carbonate (CaCO₃) would cover the corroding surface and stifle corrosion. However, most of the scale would precipitate in the filters and distribution mains leaving the main part of the distribution system unprotected².

The introduction of sodium hexametaphosphate for scale prevention in 1938 helped considerably by permitting lime-softened water plants to send water at pH greater than 10.0. Around 1940, it was found that the sodium hexametaphosphate itself was an effective inhibitor at pH values below 8.0, and being nontoxic, as well as colourless and odourless, was ideal for use with water supplies. In addition to reducing consumer complaints, this inhibitor also minimized the build-up of tubercles in the first six months after mechanical cleaning of water mains.

In the early 1950's, a sodium-zinc glassy phosphate containing 8-9% zinc was developed. This was found to be 3 to 5 times as effective as sodium phosphate glass in overcoming corrosion problems. In spite of the limitations of these inhibitors, they have been widely used in over-coming corrosion problems². In addition to these inhibitors, sodium silicate or calcium carbonate films have also been employed. Of late, a mixture of zinc sulphate, sulfamic acid and monosodium phosphate has been used for protection against corrosive waters³. Table 1 gives a few of the inorganic inhibitors commonly used, and Table 2 lists the organic ones⁵.

Among the practical methods of controlling corrosion may be included: (a) removal of dissolved exygen, (b) removal of free carbon dioxide, (c) chlorination to prevent biochemical action which influences corrosion, (d) deposition of a protective coating, (e) use of paint, enamel, tar compounds, cement linings, etc.⁴ The following discussion will be restricted to the last two methods mentioned above.

DEPOSITION OF PROTECTIVE COATINGS

Among the substances commonly employed for this purpose are (1) calcium carbonate; (2) metaphosphates and phosphates and (3) sodium silicate.

Calcium Carbonate

When one considers the deposition of a protective coating, calcium carbonate is a substance that seems to be most suitable. This compound has an excellent history of success, although failures may have been due to: (a) the presence of organic contaminants which prevent adherent, crystalline, impervious scale formation, (b) high sodium alkalinity or other dissolved solids which tend to increase the solubility of CaCO₃, (c) concurrent use of phosphates to prevent excessive scale on hot surfaces, (d) Suspended matter or biological slimes which are mechanically bound with the scale and make a porous, heavy deposit, (e) incorrect selection of chemical treatment to get a positive saturation index, e.g., the use of caustic or soda ash when lime is required, or vice versa, (f) mass precipitation of finely divided CaCO₃ instead of deposition as scale, (g) a high "index of uniformity of scaling" resulting in no protection of the cold surfaces and objectionably heavy scale on the hotter surface.

Factors which affect the deposition and stability of CaCO₃ coatings on pipe surfaces, as observed from experiments^{7,8,9} may be listed as follows: (a) A protective calcite limonite-siderite coating occurs best when the specimens are corroded, or when outside current is impressed through the specimens. (b) High flow rates are desirable for the formation of hard, durable coatings. Static tests produce soft, easily removable deposits. (c) Better protection and better-bonded, harder, tougher coatings result with solutions containing colloidal CaCO₃ than from solutions of the same pH and hardness with no colloids present. (d) CaCO₃ crystals in suspension do not have a favourable effect on the formation of coatings from super-saturated solutions. (e) High flow velocities, even if induced

by applying external energy, improve the CaCO₃ stability by bringing the protective ingredients more rapidly and in greater mass to the point of corrosion reaction. (f) Each of the three factors, viz., calcium, alkalinity and pH, usually in increasing concentrations, helps to inhibit corrosion rates. When their proportions are such that a condition of sufficient supersaturation exists with respect to calcium carbonate solubility, the tendency towards corrosion and tuberculation can be eliminated. Tuberculation occurs when corrosion is almost, but not totally, prevented by this treatment. (g) Alkalinity greater than 100 mg/l, in the absence or with low concentration of calcium, serves as a weak inhibitor in contrast to the effect of chlorides and sulphates. Inhibition is at pH 8.0 to 8.5, because the buffer capacity of the carbonate-bicarbonate equilibrium decreases 10 times near the phenolphthalein end point, relative to that at pH 7.0 and 9.5. With strongly buffered waters, the ability of corrosion products to self-accelerate corrosion is less than with weakly buffered waters. (h) Although corosion rates are lower in hard waters than in soft waters, it appears that the thickness of CaCO₃ alone is not sufficient for corrosion protection. The crystalline state of the precipitated CaCO₃, is also important. In a soft water, the precipitated iron salts also show a different structure than in hard water. (i) In the presence of greater amounts of electrolyte (i.e. hardness) colloidal iron hydroxide is more rapidly precipitated on iron surface because of the reduction in zeta. potential. This was partially confirmed by Stumm⁹ when in a water containing 205 mg/1 hardness at pH 8.4, 95 to 100% of the iron lost in corrosion was found in the surface film, whereas in softer water (hardness 117 mg/l), only 67 to 73% of the iron appeared in the film at the same pH value. (j) The amount of CaCO₃ deposited at an iron wall is dependent on the CaCO₃ saturation index, buffer capacity and dissolved oxygen in the water. In waters having positive saturation indices, the corrosionaccelerating influence of dissolved oxygen may become insignificant, because the rate of formation of protective films also increases as dissolved oxygen increases.

It should be borne in mind that the addition of CaCO₃ to water to form a protective coating is only supplementary to natural or artificial protective coating on metals. This is emphasized if we were to consider for providing a protection to a water distribution systems serving 25,000 people. Larson¹⁰ has calculated theoretically that for this population, the internal surface area of pipe network would be 17 acres and to get a deposit of 0.001 in. thickness, the amount of CaCO₃ required would be about 5.3 tons. To obtain a deposition of 3 mg/l from 3 mil. gals. a supersaturated water would take nearly 5 months. On the other hand, if 99.9% of the surface were coated by some other means, it would take only a few hours of exposure to achieve initial protection of the pipe.

Since the deposition of CaCO₃ and its success as a corrosion inhibitor depend largely on the quality of water and the interaction between pipe material and water, an uncontrolled deposit does not necessarily give a satisfactory corrosion control. A partial control over the deposition can be had by the addition of a small amount of metaphosphate. McCaulay¹¹ reports on the addition of 0.5 to 1.5 mg/l of metaphosphate to Michigan State University tap-water which gave satisfactory CaCO₃ precipitation. Good coatings were reported with metaphosphate concentration of 2.2 mg/l and calcium level as high as 1500 mg/l (as, CaCO₃). Such treatment amounts to "threshold" treatment given to lime-soda ash softened waters.

Among the few municipalities using calcium carbonate scale may be mentioned Omaha, Neb, which has laid down such linings in approximately 2 miles of 6 in. and 8 in. water pipes. McCauley process has been used, which consists of applying within 2-3 hours a protective cacium carbonate coating to the interior of cleaned iron and steel water mains. The process requires the formation of a controlled, supersaturated solution of calcium carbonate within the water that passes through the main during the coating period¹⁶.

The Philadelphia Water Department also used calcium carbonate coatings for protection of its small diameter mains. Results of a field test indicated that the 'C' value of 1500 ft. long 6 in. dia. pipe was raised from 43 to 111 after coating with CaCO₃. Further tests on other 6 in. sections showed satisfactory coatings. But microscopic examination of the coatings revealed pore spaces in the deposits. An attempt to plug these with sodium silicate (doses upto 35 mg/l) was not successful. However, 60-100 mg/l of sodium silicate alone gave very satisfactory results¹⁶.

Jersey City reports that within 6 months from the application of McCaulay's process to its 6 in. pipe line, the calcite lining disappeared on account of the aggressive nature of the water. As long as the lining existed, 'C' value is reported¹⁷ to have been maintained at about 115.

The Borough of Morrisville, Pa. has reported successful application of the Medusa gray, Portland cement-calcite lining process. A total of 2800 ft. of 4 in. C.I. main was lined, raising the average 'C' value from 41 to 115. The lining is reported to have held up on account of increase in the CaCO₃ saturation index to near stability, as the water was originally slightly corrosive.

Phosphates and Metaphosphates

Among the anodic inhibitors, metaphosphates and phosphates are the two groups of compounds very commonly used in water supply systems. They are also useful in industrial water treatment. Originally used for preventing "red water" trouble, the phosphates have also found use in maintaining pipeline carrying capacity, in new as well as mechanically cleaned pipelines. They are known to give the following added benefits: (a) precipitation of iron already in the water or that due to corrosive action is prevented, (b) large tubercles are not formed in the mains, leaving the pipe surface smooth, (c) the products of corrosion of small water piping in buildings do not collect and clog the piping⁴.

When sodium hexametaphosphate was first introduced to the water industry in 1938, it helped by permitting lime-softened water to be conveyed at pH greater than 10. At lower pH values, lower concentrations than those required for complete scale prevention were used to ensure uniformity of the CaCO₃ coat. However, two years later, it was found that this compound was also an effective corrosion inhibitor when used alone at pH values below 8.0. Using from 50 to 100 mg/l of glassy phosphate during cleaning and flushing, followed by a continuous dose of as much as 10 mg/l for several weeks after the main was recommissioned, was found to minimize build-up of tubercles after mechanical cleaning of water mains².

Although the hexametaphosphate can protect ferrous metals even at pH 5.0, a more effective film is formed at pH values below the stability pH than in waters with a positive Langelier index. A small amount of calcium (as Ca⁺⁺) is required in the water to permit formation of a protective film. Usually 1 mg/l of calcium is required for every 2 mg/l of phosphate. The feed rate of the inhibitor for a given system depends upon volumetric flow rate of water, but the feed rate should be controlled to give a metaphosphate residual of 0.5 to 1 mg/l at the extreme ends of the system. The treatment is effective against the usual corrosive constituents like dissolved oxygen, carbon dioxide, sulphates and chlorides. The exception is hydrogen sulphide which must be removed by aeration and/or chlorination.

Glassy phosphates have their limitations. It takes a fairly long time to develop a satisfactory film under conditions of high temperatures or low, intermittent flows. Although the film does not build upon itself and impede flow, it is not permanent, and continuous feeding is necessary to maintain

it. They are useful only at higher turbulent velocities and at increasing concentrations. They are not at all effective under stagnant conditions as in service mains and dead ends. In hot water systems, corrosion rates are greater than in cold water systems. Recirculation of water improves the effectiveness of the inhibitor in the hot water system, but not in the water tank, due to low velocity of water.

It is known that water mains which are cleaned after a long service are susceptible to very rapid corrosion rates due to exposure of the fresh metal. Glassy-phosphates are useful in this operation and in maintaining protective film after cleaning. Usually, a higher than normal dose (upto 10 mg/1) should be maintained in the water used to force the cleaning tool through the main and in all of the flush water. From 2 to 5 mg/1 of glassy phosphate is added at least ten days before cleaning, to ensure that the system contains a good metaphosphate protective film. A high concentration used during cleaning is followed by 10 mg/1 for the first week after cleaning, before return to normal feed level for continuing treatment.

A zinc-bearing phosphate glass (containing 8-9% zinc), developed in the early 50's, was found to be 3 to 5 times as effective as sodium phosphate glass in overcoming corrosion in water systems. In this application, concentrations equal to twice the total hardness for soft waters, and upto a maximum of 50 mg/l for medium and hard waters should be used during cleaning and flushing. This should be followed by 5 to 10 mg/l dose for at least a week. Continuous treatment with regular glassy phosphate should then be adequate to maintain the film in good condition throughout the distribution system. A drawback of the zinc-bearing phosphate glass is that it takes more than 24 hours to dissolve this compound in water at temperatures above 10°C. At lower temperatures, it may not dissolve at all. Further, feed solutions of more than 1% are seldom stable.

For municipal water treatment, sodium hexa metaphosphate in the form of broken glass platelets is normally specified. The platelets are easily soluble in water. A strength of 1 to 2 lbs. per U.S. gallon of water is used for feeding. Since concentrated feed solutions are corrosive to ordinary iron and steel in the absence of sufficient calcium for film formation, corrosion-resistant equipment should be used. Gravity feed or pump feed can be used. If pumps are used, they should have stainless steel or plastic parts. Feed tanks, connecting lines and fittings should be of stainless steel, plastic, rubber, plastic-lined, rubber-lined steel, or ceramic. If iron and steel feeding equipment must be used, reasonably good service life can be obtained by adjusting the feed solution with soda ash or caustic topH of 9.5.

A few case histories of the use of glassy phosphates are given below:

A small municipality near the Atlantic coast, treating about 500,000 gpd of water by conventional method was faced with severe corrosion problem. The water had a pH of 6.1, hardness of 16 mg/1 to 15 mg/1 of sulphate ion. Continuous treatment of the treated water with 2 mg/1 of sodium hexametaphosphate failed to eliminate the problem of corrosion. Even when the dose was increased to 5 mg/1 only partial success was achieved. However, only 1 mg/l of bimetallic glassy phosphate worked better than 5 mg/l of sodium hexametaphosphate, and helped to considerably reduce the consumer complaints².

Gorham, Me. reports satisfactory maintenance of pipeline carrying capacity with the use of sodium hexametaphosphate. 'C' value was found to increase from 56 to 120, and was maintained therefor about 14 months¹⁸.

The experience of a water utility in Western Pennsylvania indicates that a starting dose of 2 mg/l of glassy-phosphate, reduced in steps of 0.25 mg/l per week, gave good results with raw river water (having 86 to 103 mg/l average hardness, 4 mg/l of manganese and 2 mg/l iron during certain seasons of the year). This water was treated to give not more than 0.05 mg/l of manganese and 0.1 mg/l of iron. For a daily flow of 18-20 U.S. mil. gal., a minimum glassy phosphate feed rate of 1.25 mg/l was necessary. The same source, serving a smaller community, required from 3 to 3.5 mg/l of glassy phosphate to maintain satisfactory distribution of water¹⁹.

Charlosville, Va. required cleaning of its water main (17 mile length, 18 in. dia. C.I.) every 4 to 6 months due to corrosion problems. Little benefit was obtained by liming and chlorination of the water to maintain pipeline carrying capacity. However, with only 3 mg/l of glassy phosphate, the pipe cleaning interval was found to increase to nearly 11 months. In addition to providing protection, it was also found unnecessary to run the booster pump on the line during peak demand periods, which used to be necessary before glassy phosphate treatment²⁰.

O'Hara²¹ describes the effectiveness of glassy-phosphate treatment in overcoming red water and tubercle buildup at Arlington, Mass. Only 2 mg/l of this chemical was found necessary. After 8 years of service, the pipeline surface was found to be in good shape.

Sodium Silicate

The treatment of public water supplies with sodium silicate is restricted largely to waters softened by the cation-exchange process, because an increase in hardness can thereby be avoided. Small amounts of sodium silicate (Na₂O. 3.25 SiO₂ or Na₂O. 2 SiO₂) deposit a dense, adherent, but slightly permeable film. An initial dose of 12 to 16 mg/l as SiO₂ is given to the water for about a month. The dose is reduced thereafter to the amount necessary to maintain a residual of 1 mg/l in remote parts of the distribution system⁴.

The protective action of sodium silicate on ferrous metals is, to a certain extent, due to the fact that being a salt of weak silicic acid and strong base (sodium hydroxide), it renders the solution distinctly alkaline. It is believed that silicates form a thin self-regenerating film on the metal surface which practically suppresses corrosion. Such a film may form as a result of precipitation of silicic anions by metal ions or by corrosion products. Another viewpoint suggests that the protective film is produced by the mutual coagulation of particles of the metal hydroxides and silicic acids, deposited on the metal surface. Silica is not removed from water until solid corrosion products form on the pipe surface. Zinc hydroxide (such as forms in G.I. Pipes) takes up silica by chemisorption, resulting in the formation of an adsorption compound. Cupric and ferric hydroxides, and magnetite also remove silica, but the mechanisms appear to be different²².

COATINGS AND LININGS

The action of organic and inorganic inhibitors is restricted to the inner surfaces of water pipes and conduits. But for internal as well as external corrosive conditions, coatings and linings of various materials are chosen to protect the pipes. They interrupt both anodic and cathodic reactions by preventing escape of cations and denying access of water and oxygen to the metal surface. Metallic coatings (e.g., zinc, tin, chromium) or non-metallic coatings (e.g., paints, cement, bituminous materials, plastics) are suitable.

Cement Mortar Linings: In the past, pipes used for conveyance of water were installed as they arrived from the mold. No attempt was made to protect the surface from corrosion. However, loss in carrying capacity of the pipe was among the first effects which compelled the water engineer to look into this problem. As early as 1865, the French Academy of Sciences recommended the use of a cement lining in pipes for maintaining their carrying capacity. A little later, bituminous coatings, usually molten coat-tar pitch, came into use. These coatings protected the pipe surface effectively in hard waters, but in soft and acid waters, problems arose with "red water", and reduction in carrying capacity continued to take place. In the 1870's, cement-lined and coated wrought iron pipe, consisting of a 20-gauge wrought-iron shell with a cement lining 1/2" thick inside and out was used. Their useful life was 20 to 25 years. The first² cement lined cast iron pipe was installed in U. S. A. in 1922. With increasing use of plastic materials, the pipes can be given adequate protection from corrosive water and aggressive soils.

Literature cites instances of successful operation of cement mortar linings. A survey extending over 39 years of observations shows that these linings could effectively maintain the Hazen-William coefficient at an average of 140, equivalent to that of a new pipe surface. The thickness of the lining varies from 1/16 in. to 1/4 in. Tuberculation was prevented in very soft and acid waters. Where cement linings without a seal coat were applied, low cohesive strength was found in the linings after 30 years of use, but the pipe metal was adequately protected 12.

Among the processes used for obtaining suitable cement mortar linings on the inner surfaces of the piplines, Tate process was developed in Australia and was first used in the U.S.A. in 1939. It consists of packing one end of the pipe to be lined with enough cement mortar to give a predetermined thickness of lining. Then a mandrel is drawn through the pipe with a cable which is placed in the pipe before cement mortar packing. The mandrel pushes the mortar ahead and packs it in the connections, hydrant branches and services. Therefore, all these must be disconnected before starting the process. Lining thickness¹² varies from 3/16-5/16 in.

With the development of machinery for applying cement mortar by using centrifugal force, it has been possible to line considerable lengths by the centrifugal process. The cement lining which is actually a 1:2 Portland cement mortar, is applied in thickness of 1/8" upto 12" pipe, 3/16" upto 24" pipe and 1/4" upto 48" pipe. A plus tolerance of 1/8" is allowed on all pipe sizes and of 1/4" on all fittings. The thickness is tapered slightly for not over 2 inches at each end of a pipe length. Usually, curing of the lining is done by applying a bituminous seal coat which retains moisture. No injury is done to the lining by cutting the pipe or drilling holes in it¹³.

Cement mortar linings can be given to cast iron as well as steel surfaces. Defects in lining can be kept to a minimum by adequate inspection during construction of the pipe line. Corrosion of the metal is prevented even in the presence of free oxygen and chlorides, provided the oxygen is not trapped against the metal. The hydroxide ion from calcium hydroxide in the cement is credited with the formation of an iron oxide film on the metal surface, thereby tending to electrically isolate the metal from its environment. Under conditions where cathodic interference exists, a sound reinforced concrete structure may be protected by other means in addition to cement mortar linings¹⁴.

In spite of its widespread use, a cement mortar lining has its own drawbacks. As in the Tate process, all branches, hydrants, etc., on the line being treated must be disconnected to prevent the mortar packing itself into the branches. In areas where extensive excavation is not possible, or where severe underground congestion by other services exists (as is common in big towns and cities),

application of conventional cement mortar linings may be very difficult¹⁵. Further, under severely corrosive conditions, it may be necessary to add substances like sodium silicate or aluminium and magnesium chloride to the cement mortar to get an adherent, porefree lining surface.

Typical examples of the use of cement mortar linings are given below:

A 16 in. cement lined pipe from Champague, I.l.l. was found to be in excellent condition after 22 years of service carrying hard water. The flow coefficient was 145, equivalent to new pipe. The cement lining was not seal coated¹².

As against this, the cement lining of a 12 in dia 29 year old pipe carrying soft, tuberculating water was found to have a roughened, saudy texture. The flow coefficient was 137 and the lining had too low cohesive strength 12.

A 16 in. cement lined pipe, 6 miles long, in Catskill, New York, after 25 years of continuous service in a soft acid water, was found to have retained the lining in a perfect condition; the flow coefficient¹² (including valves and fittings) was 135.

An 8 in. dia cement lined pipe carrying raw water for 19 years showed a 'C' value of 129, on account of a thin bacterial slime growth, coating the pipe surface. The raw water had a hardness of 13 mg/l, a total alkalinity of 8 mg/l and pH of 5.8 to 6.7. This water was very aggressive and highly tuberculating. The 'C' factor was restored to 142 after treatment with 100 mg/l chlorine for 24 hours and thorough flushing¹².

Cement mortar linings have been extensively useful in reconditioning water mains after cleaning, as is seen from a few examples which follow:

Nor folk, Va, had many miles of unlined C.I. mains, their age varying from 30 to 85 years at the time of reconditioning. The 'C' value varied from 40 to 70. These, along with other pipes varying in diameter from 30 in. up to 16 in., were restored to their original carrying capacity by cement mortar linings applied by the centrifugal process¹⁵.

The same city restored, in 1956, approximately 10 miles of 20 in. and 16 in. C.I. pipes with cement mortar linings. The carrying capacity was increased by 125 per cent, at a total cost only 25 percent of that for total replacement.

In 1944, the city of Rochester, N.Y., lined 38,000 ft. of 36 in. dia. wrought iron pipeline, which was installed in 1873 but was abandoned in 1934 due to leakage¹⁵.

Bituminous Coatings and Linings

Although coal-tar was mentioned in an English patent around 1861, its first use to protect water pipe in the form of coal-tar enamel was made in New York in 1914. It had a softening point usually between 180°F and 200°F and a mineral filler content of 25-35 percent. The original coatings were found to crack at temperatures below 30°F and sag above 100°F temperature. However, during 1928-32 considerable research was done to remove these defects. This resulted in what is commonly called "Plasticized pitch"²⁴.

Pipes of large diameters are obtained by using steel plate, which requires corrosion protection more than cast iron, on account of its smaller thickness. Steel plates have mill scale on their surfaces when they are rolled into pipes. This is removed thoroughly and the pipe is coated with bituminous enamel. Scars or other defects in the coating caused by handling and laying of the pipe must be removed before putting the pipe into commission¹³.

Bitumastic enamel, a coal-tar with 20% or more inert filler is a good protective agent. The pipe surface, after cleaning and drying, is first coated with a priming coat and then hot enamel is applied by hand brushing to 1/16" thickness. Graphite paint, water-gas and coal-tar paint and asphalt have been used 1/16.

Bitumastic enamel may also be applied hot, centrifugally to the pipe interior, the usual thickness being 3/32". In another process, the lining is applied using the principle of electrophoresis. This process is similar to electroplating and involves filling the pipe with the coating emulsion (which is a stable aqueous suspension of water-washed bitumen). A D.C. generator applies voltage between the coating material and the pipe. As current flows, bitumen particles travel towards the anode (the pipe wall) and adhere to it, forming a dense layer. An indication that the deposit has developed is that the current passing through is reduced. The process is useful for pipes upto about 16 in. diameter¹⁵.

The use of bituminous coatings on the interior and exterior surfaces of pipe lines has proved its value as is evident from the following two case histories:

In 1937 plasticized coat-tar enamel was applied centrifugally to a steel pipeline on the Los Angeles aqueduct. A part of this line formed a siphon crossing Santa Ana river, the head ranging upto 485 ft., and pipe diameter ranging from 116 in. to 138 in. The enamel thickness was 3/32 in. The line was opened for insertion of a valve in 1966. It was found that the enamel surface had developed a thin film of organic growths which was easily removed with brush and water. Apart from this growth, there was no sign of the enamel deteriorating, sagging, or checking. The same line was also given a coal-tar enamel coating to the exterior surface under the guniting in sections where the soil was found to be corrosive. Straight sections of the pipe were coated with enamel by centrifugal casting, but bends, branches and field joints were coated by daubing²³.

Cleveland, Ohio, undertook the first bituminous lining operation in its water distribution network in 1949. Pipes of 6 in. and 8 in. dias. were coated using the principles of electrophoresis as explained above. Flow tests carried out on these lines showed that the 'C' values which ranged from 39 to 93 before lining were brought up to a range of 112 to 127 and were maintained there as revealed by flow capacity tests of the lined pipes. As the results of these tests were encouraging, further lining work was undertaken, and by 1957, about 80,000 feet of lines from 6 in. to 16 in. dia. were lined 15.

Plastic Linings and Coatings

Internal Application

Since about 1945, considerable work has been done in applying plastic linings in the rehabilitation of small diameter steel water mains. Solution type vinyls were used in the earlier application but difficulties were experienced with washouts as the evaporating solvents collected and condensed down the line during the air-drying cycle. Development of high-solids, catalyst cured modified epoxy coatings has virtually eliminated this problem²⁶.

The main problem in internal application is the attainment of a thoroughly clean, dry metal surface. Use of various solvents, mechanical scraping, alkaline, acid and water-wash have been done on a crude oil pipeline before lining. The lining is then applied by extruding a film around the follower plug passing through the line²⁶.

Instead of applying a plastic film, it is much easier to apply the plastic material in the form of an epoxy coat, the details of which are given elsewhere in this volume. Hence, they are not dealt with here.

External Application

Nearly 15 years ago, tests were initiated in the U.S. by Cast Iron Pipe Research Association (CIPRA) using polyethylene (PE) tubes and sheet material to protect C. I. Pipes. Results indicate that a losely applied PE tube material provides effective protection in corrosive soils. PE tube material about 8 mils thick is available in tube form, in precut lengths and various diameters, so that approximately 1 ft. overlap at joints is possible²⁷.

In use, a suitable length of the PE tube material is slipped over the end of a length of pipe which is raised above ground at trench side. The pipe is then lowered, jointed, and then I ft. excess length of the material is slipped to overlap or underlap the adjacent tube. The excess material is folded over the top of the joint and held there by plastic-backed adhesive tape about 2" wide. No attempt is made to obtain watertight joints at overlap areas, because intrusion of water under the plastic does not significantly affect the protection afforded by PE material. Fittings, valves and stop cocks with irregular shapes are wrapped or packed with a section of the PE material split to form a flat sheet, held in place with plastic tape²⁷.

Corrosion of the external surface of a pipeline depends very much on the nature of soil through which it passes. Artificial environment such as cinder-fills, municipal dump areas, or places where industrial wastes have been used as fill, can be quite corrosive. Certain natural soils such as saline marshes, wet alkaline soils, peat areas and some types of clay and gravel mixtures can also contribute to corrosion. Wagner²⁵ describes the experience in the use of plastic wrap as protection against external corrosion. These test sites selected were (a) cinder-fill in Birmingham, Ala, (b) tidal-salt marsh in Atlantic city, N.J. and (c) muck in Everglades, Fla. Samples of pipes wrapped with polyethylene, plastic film and held in position with polyethylene adhesive tape were buried at these sites and were inspected after 9 years. Specimens sealed with tape showed no rusting whereas the loosely wrapped specimen showed only a few spots of rust. There were no pits on the wrapped pipe surface, while the bare surface showed pits up to 100 mils deep.

The success of this system is attributed to the rapid stagnation of the water which seeps between the polyethylene film and the metal surface. The water loses its dissolved oxygen content through reaction with the iron surface, thereby becoming deficient in the chemical constituent necessary to continue corrosion.

In the case of cinder-fill, the polyethylene film protected the pipe by acting as a physical barrier between the carbon-bearing cinders and pipe metal, thereby preventing the formation of galvanic cells.

The film was also found quiet effective in protecting pipes from corrosion due to stray currents in the soil²⁵.

Although the PE film wrap is suitable, it may not be as commonly used as coal-tar enamel on cement mortar; however, it appears entirely feasible to provide 10, 15 or 20 mil coatings and linings to give necessary protection and still be competitive in cost.²⁶

In spite of these advantages and ease of application, polyethylene film wraps have certain disadvantages: (a) the film is easily damaged, (b) if it is sealed at both ends, determining the location of a leak is difficult and (c) the use of a pipe locator to follow a main in the street is not possible, as the film has high dielectric strength and it stops the current from completing the circuit²⁶.

Like the polyethylene film, synthetic rubber is also used for fighting corrosion, but it is more suited to coat chemical process tanks and vessels. A limited amount of data on neoprene, thiokol and other synthetic rubber linings indicates that these may prove costly in comparsion with other types of coatings. Neoprene is usually applied by one of the three methods: (a) cold application of liquid neoprene, (b) hot vulcanization and (c) adhesive bonding of cured sheet stock. Thiokol is used mainly for protection against marine environment and is asually not preferred for protecting water lines.

An example of the use of rubber coating for protection against corrosion is that of the water treatment plant in Morgan City, Louisiana²⁸. The plant has a chlorinated rubber coating system consisting of a 1.2 mil dry film thickness of white primer on field sand-blasted metal, two intermediate coats of white undercoater each of 2 mil dry film thickness, and a 1 mil coat of blue enamel. Steel structure thus protected consists of primary mixing and reaction chamber, secondary reaction separation zone, sludge scraper mechanism, radial launders with submerged orifices and columns and beams, supporting control mechanisms and access walkways in filters, inlet water distribution assemblies, washtroughs, backwash siphons, and platforms; exterior surfaces of control centre equipment were also treated similarly.

Non-submerged C.I. Pipe and all valves were given two coats of synthetic resin and titanium pigment sealant followed by two coats of impact resistant alkyed based resin high gloss enamel. Columns and elbows on raw water intake pumps were coated inside and out with coal tar epoxy primer and two coats of coal tar enamel.

Table 3 gives a comparative statement showing the application of plastic and non-plastic lining materials²⁶.

Table T Inorganic Inhibitors

Name	Approximate concentration	Corrosion environment	Metallic system Steel	
Calgon	Small amount	Water systems		
Potassium dihydrogen-				
Phosphate + Sodium nitrite	0.5	Sea water	Steel	
Potassium permanganate	0.10	0.3% NaOH solution	Aluminium	
Sodium benzoate	0.5		Mild Steel	
Sodium hexametaphosphate	0.002	Water about $pH = 6.6$	Lead	
Sodium metaphosphate	Small amount	Ammonia	Mild steel	
Sodium nitrite	0.005	Water	Mild Steel	
Sodium nitrite	0.20	Sea water & distilled		
		water mixture	Mild Steel	
Sodium orthophosphate -	ī	Water, $pH = 7.25$	Iron	
Sodium silicate	Small amount	Sea water	Zn, Zn-Al allovs	

Table 2 Organic Inhibitors

Name	Approximate concentration,	Corrosion environment	Metallic system
Ethylaniline	0.5	HCl solution	Ferrous metals
2-Mercaptobenzo-thiazole	1	HC1 solution	Iron & Steel
Morpholine	01.2	Water .	Heat exchange systems
Phenyl-acridine	0.5	H _a SO ₄ solution	Iron
Pyridine + Phenyl-hydrazine	(0.5 + 0.5)	HCI solutions	Ferrous metals
Quinoline-ethiodide	0.1	in HaSO	Steel
Rosin-amine-ethylene oxide	0.2	HCl solution	Mild steel.

Table 3 Comparison of plastic and non-plastic linings and coatings26

Material	Use	Film thickness mils.	Place of application	Pipe size in.
1. Plastic Linings and Coatings	and the second section of the section of t			
Phenolic, baked	L	5-7	Shop	2-12
Vinyl, Solution type	C&L	5-15	Shop or field	Any
PVC sheet		1/16-3/16 in.	-do-	Large
Polyethylenes, extruded	C	0.025 in.+	shop	4½ in max.
Vinylidene chloride copolymer	L	0.16-0.25 in.	-do-	2
Tetrafluoroethylene	l.	1/8 in.	-do-	Small
Epoxy, nonbaking	C & L	5-7	Shop or field	Any
Epoxy, baked	C&L	5-7	Shop	Any
Epoxy, coal tar	C&L	25	Shop or field	Any
Neoprene, liquid	L	20-30	-do-	Large
Neoprene, sheet	L	1/16-3/16 in.	-do-	Any
Polyethylene tape	C	12-20	Field	-do-
PVC tape	C	10-20	-do-	-do-
2. Nonplastic linings and coatings				
Coal-tar enamel	L	3/32 in.	Shop	4 ÷
Coal-tar enamel with 15.lb. asbestos felt and kraft paper	C	-do-	Field (hand applied)	any
Cement mortar	1 & C	1/8-1 in.	Shop	4.+

Note: L=Lining; C - Coating.

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