

port, well substantiated by other studies, evaporation values were calculated for the critical drought period, 1915-19. Table 1 shows the monthly values for 1916. The average monthly values, in inches, were multiplied by the reservoir surface area and the result converted to acre-feet. All of the yield studies started with the assumption of a minimum pool of 50,000 acre-ft in November 1915.

In addition to computing evaporation losses, corrections for rainfall on the reservoir and for seepage loss through the bottom of the impoundment were made in arriving at the desired storage volume for each of several assumed rates of supply. The seepage value was arbitrarily set at 200 acre-ft per month, taking into consideration the nature of the underlying formations. As the rate of movement through sands of the type involved has been found by the US Geological Survey to be extremely small, the seepage loss figure adopted is believed conservative.

It was determined that, with a drought period like the one discussed, an average annual demand of 140 mgd required 99,600 acre-ft of effective

storage; 150 mgd, 108,900 acre-ft; and 160 mgd, 116,100 acre-ft. To each of these figures must be added a minimum of 50,000 acre-ft of dead storage, desirable primarily to maintain the best possible quality of water during dry periods.

#### References

- Review of the Hydrologic Studies, Proposed San Jacinto Reservoir, Horner & Shifrin, Cons. Engrs., St. Louis, Mo. (1944; unpublished).
- LINSLEY, R. K., JR.; KOHLER, M. A.; PAULIUS, J. L. H. *Applied Hydrology*. McGraw-Hill Book Co., New York (1949).
- Possum Kingdom Project—Brazos River Basin. Special Report on Hydrologic Studies. US Army Corps of Engrs., Washington, D.C. (1937; unpublished).
- Buffalo Bayou, Texas, Flood Control Project. Special Hydrology Report. US Army Corps of Engrs., Washington, D.C. (1938).
- Report on Storm of Nov. 21-27, 1940 and Dec. 1-16, 1940. Special Supplement No. 1. Hydrologic Unit, US Weather Bureau Regional Office, Fort Worth Tex. (1941).
- MEYER, A. F. Evaporation From Lakes and Reservoirs: A Study Based on Fifty Years' Weather Bureau Records. Minnesota Resources Commission, St Paul, Minn. (Jun. 1942).

## Mechanism of Corrosion Inhibition by Sodium Metaphosphate Glass

By James C. Lamb III and Rolf Eliassen

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phosphate served to stabilize this protective film.

Also in 1952, Hatch (4) found that metaphosphate acted preferentially at the cathodes of corrosion cells. He concluded that it should be classed as a cathodic inhibitor, and that the inhibitory action was due to the electro-deposition of a film of calcium metaphosphate complexes on the cathodes.

In 1946, Evans (5) classified metaphosphate as an anodic inhibitor, on the basis of unpublished results. In 1951 the same author (6) stated that it was probably a cathodic inhibitor and mentioned the possibility of colloidal action. No data were presented at that time.

In order to obtain a proper evaluation of the efficiency of metaphosphate glasses as corrosion inhibitors, it is necessary to determine the inhibitory mechanism. Such knowledge should lead to a more accurate concept of the variables affecting the action of the chemicals, and should result in increased efficiency and economy in their use for the control of corrosion in municipal and industrial water systems. The research reported in this paper was undertaken for the purpose of determining the mechanism by which a

sodium metaphosphate glass inhibited the corrosion of iron in water.

#### Continuous-Flow Equipment

The limitations of batch testing procedures have been pointed out by Hatch (7). Of particular importance is the fact that the total amount of inhibitor available to the metal is limited to that present in the beaker, whereas, under continuous-flow condi-

tions, there is a constant supply of inhibitor to the metal surface. The effect of velocity on the rate of corrosion of iron in water has been known for many years (5, 8, 9). It has been found (7) that the effect is even more pronounced in metaphosphate-treated waters.

The experimental equipment used in the initial phase of these studies was of the continuous-flow type, as shown

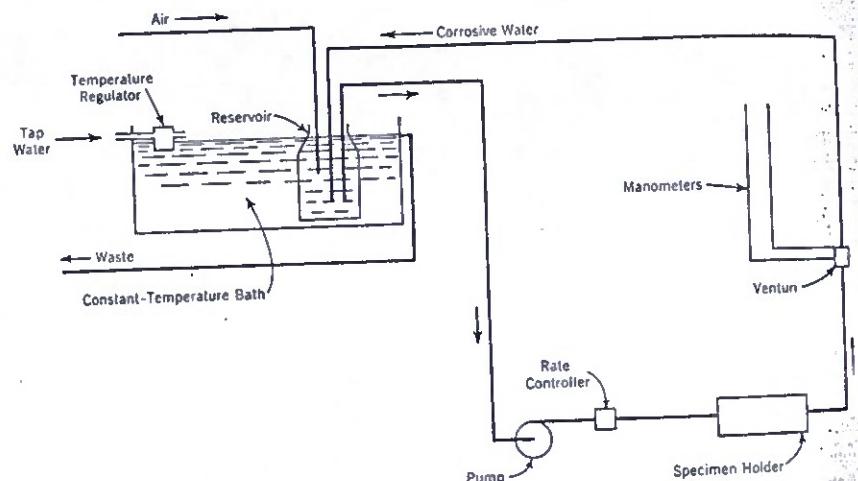


Fig. 1. Flow Diagram of Test Equipment

The reservoir is a 5-gal glass carboy. The temperature was  $27^{\circ}\text{C} \pm 1^{\circ}\text{C}$ . Water was circulated at a constant rate.

pipes in the system were made of pyrex tubing or rubber hose. Hence, the water did not touch any metal in the test system, with the exception of the stainless-steel pump and the corroding specimens.

Figure 2 shows the specimen holder which permitted the removal of specimens at various times during a run. Each specimen holder was designed for eight galvanic cells. The use of baffles

May 1954

in the holder resulted in the formation of eight identical compartments. This arrangement provided similar flow conditions in the vicinity of the two electrodes of each galvanic cell.

The specimens were machined to a diameter of 0.900 in. and a thickness of 0.25 in., in order to permit them to fit into the special cups used with standard radioactive counting equipment. The face to be exposed to the water was prepared in accordance with

trodes on opposite sides of the specimen holder were normally short-circuited by means of small sections of wire, to form galvanic pairs of anodes and cathodes.

When it was desired to remove specimens in order to determine the deposit of metaphosphate, the flow through the system was stopped. The rubber hoses were pinched shut to prevent loss of water from the system, and two specimens, comprising a galvanic

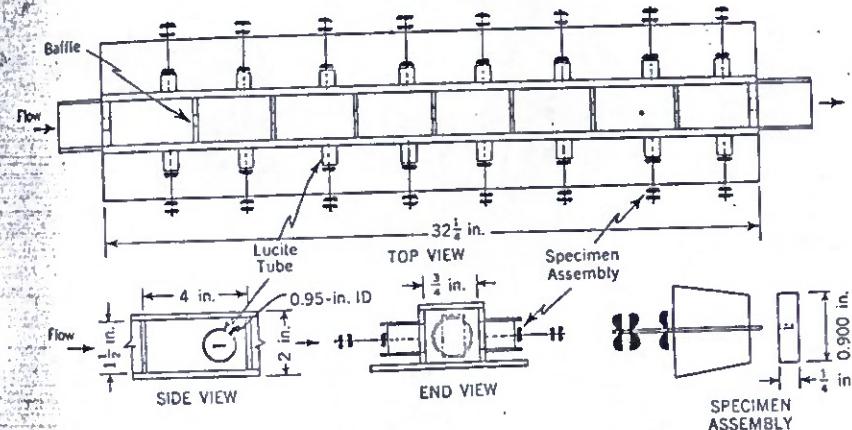


Fig. 2. Specimen Holder

This arrangement provided similar flow conditions in the vicinity of the two electrodes of each of the eight galvanic cells in the holder.

standard laboratory techniques for handling corrosion specimens. All of the metal, except for this face, was waterproofed with a mixture of beeswax and paraffin. Bolts were passed through rubber washers and screwed into the tapped holes on the back faces of the specimens. The specimens were mounted in the holder by inserting these assemblies into lucite tubes, placing the exposed faces flush with the inside of the lucite channel. The elec-

#### Radiochemical Analyses

The quantities of metaphosphate deposited on the anodes and cathodes were usually very small. The use of radioactive tracer techniques made it possible to determine the amounts of

May 1954

## CORROSION INHIBITION

these deposits without removing the protective films from the metal.

The metaphosphate used in these tests was a glass, prepared in the laboratory from phosphoric acid and sodium carbonate, with a  $P_2O_5$  content of 67.5 per cent. This approximates the makeup of a commercial product used for the control of corrosion in potable-water systems. A trace amount of radioactive phosphorus ( $H_3PO_4$  containing  $P^{32}$ ) was added to the mixture at the time of preparation. Levels of radioactivity in the test water were adjusted to the desired value in all runs by diluting the radioactive metaphosphate glass with stable metaphosphate glass of identical composition. Dilution was accomplished by adding appropriate amounts of stock solutions of the two glasses to the synthetic tap water in the reservoir.

Radioactivity, measured in counts per second per milligram of metaphosphate in solution, was determined at the beginning of each run by counting three samples of the test water. The counting equipment used for the radiochemical determinations was a mica window type of Geiger-Muller counter, with automatic sample changer. This equipment has been described in a previous paper (10). The same counter was used throughout all tests.

After removal from the test assembly, the specimens were placed in nickel-plated counting cups and counted three times. Corrections were made for background, geometry, and decay of the radioactive phosphorus. The amount of deposit on each specimen was determined by relating the corrected counts per second of the specimen to the counts per second per milligram of metaphosphate in the corrosive water. All deposits were ex-

pressed as milligrams of metaphosphate per square decimeter (sq dm) of apparent metal surface.

These techniques did not permit differentiation between metaphosphate and orthophosphate. Because both types of chemicals are used as corrosion inhibitors, and because metaphosphate reverts to orthophosphate, there may be some question whether the protective film consisted of the latter. There are several reasons for believing that it was the metaphosphate which was of primary significance in these tests.

The stock solutions of metaphosphate were prepared immediately preceding each series of runs and were kept under refrigeration until used or discarded. Analyses of the reversion characteristics of the metaphosphate showed that water dosed with 50 ppm would contain less than 1.5 ppm of reverted metaphosphate at the beginning of any run, and less than 5 ppm after 6 days at the temperature of the experiments. Film deposition studies conducted several hours apart, using the same stock solutions, did not show variations in the rates of deposit, which would be expected if the reverted chemical were the primary source of the deposited material.

The protective films on a few samples were stripped from the metal with acid and analyzed chemically for metaphosphate and orthophosphate content. Approximately 70 per cent of the chemical was found to be present in the form of metaphosphate. As the use of acid radically increases the rate of reversion of metaphosphate, it can be presumed that the ratio of this material in the film was considerably higher than 70 per cent before removal from the metal.

Although both metaphosphates and orthophosphates inhibit corrosion, their characteristics are quite different. Orthophosphates are classified as anodic inhibitors (5, 8). As it has been shown that metaphosphates are cathodic inhibitors (2-4, 6, 11, 12), it follows that the inhibitory action of these chemicals could not logically be presumed to be due to orthophosphate derived from their reversion.

#### Film Deposition Studies

The purpose of these studies was to investigate the deposition of metaphosphate on the cathodes and anodes

dissipated within a period of 12 hr after the beginning of the run. The rate of flow through the specimen holder was regulated to produce a velocity of 1 fpm.

As pickled specimens having an extremely high initial rate of corrosion were employed in this study, it was expedient to use higher concentrations of metaphosphate than those normally employed in practice. Such a procedure may be justified as long as no attempt is made to evaluate the quantitative efficiency of this chemical on the basis of these test results. The many papers by Hatch and Rice have indicated that qualitative results obtained with a 50-

TABLE I

Composition of Synthetic Tap Water

Chemical	Concen-tration ppm	Ion Concentration—ppm					
		Mg <sup>++</sup>	Ca <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
MgSO <sub>4</sub>	34.65	7.00				27.65	
CaSO <sub>4</sub>	27.09		7.98			19.11	
CaCl <sub>2</sub>	39.12		14.12				
NaHCO <sub>3</sub>	96.30			26.36	25.00		69.94
Total		7.00	22.10	26.36	25.00	46.76	69.94

as a function of time under continuous-flow conditions. Two identical continuous-flow systems were operated in parallel. A synthetic tap water with the composition shown in Table I was used in order to prevent variations in the chemical characteristics of the test waters during the different runs, and to maintain an average pH value of approximately 8.0. The total volume of water in each test system amounted to 20 liters. In order to minimize biological activity, the water was dosed with 10 ppm of chlorine at the beginning of each run. The chlorine residual in the test water, was completely

ppm concentration of metaphosphate in the laboratory are comparable to those obtained with concentrations of 2-5 ppm in actual pipelines.

Galvanic cells of steel and stainless steel were used to facilitate analyses of the action of metaphosphate on the individual electrodes of a corrosion cell. The use of stainless-steel cathodes minimized the introduction of foreign metal ions into the test solution. Although the anodes and cathodes were separated by the width of the lucite cell, the action of metaphosphate on the two electrodes of a galvanic cell of this type should be similar qualitatively, but not

May 1954

quantitatively, to its action on electrodes located on the surface of a single piece of metal, as in a pipe. This concept is correct, provided that the inhibitory action does not involve direct chemical reaction between the inhibitor and the metal to any significant degree, a matter that will be discussed in a later section.

Figure 3 shows the results of two runs made under identical conditions, but in two separate continuous-flow systems, each having 50 ppm of metaphosphate in solution. The curves rep-

resented their presence may be attributed to adsorption or reaction between the metaphosphate and the corrosion products on the anodes. Subsequent polarization studies (11) showed conclusively that the smaller deposits on the cathodes were responsible for the inhibitory action of the metaphosphate. For this reason, only cathode film formation will be discussed in this paper.

From the curves in Fig. 3, it may be seen that the amounts of metaphosphate deposited on the cathodes were extremely small, possibly approaching a

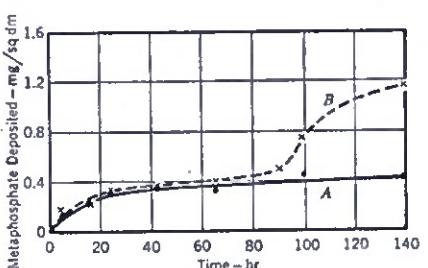


Fig. 3. Metaphosphate Deposition on Cathodes

The curves show the results of two runs made under identical conditions, with 50 ppm metaphosphate in solution.

resent the rate of deposit of metaphosphate on the stainless-steel cathodes of galvanic cells. Values similar to those shown in Curve A of Fig. 3 were obtained in other runs using 20 ppm of metaphosphate instead of 50 ppm, and in runs having widely varying levels of radioactivity in the test solutions. The deposits on the anodes varied erratically and were 20–100 times as great as those on the cathodes. As these very heavy deposits were not obtained in other tests using platinum anodes in impressed-current cells, it is

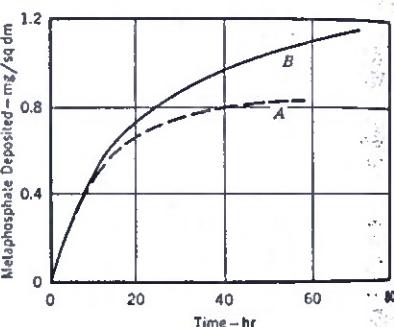


Fig. 4. Metaphosphate Deposition (Reused Water)

Water from the runs in Fig. 3 was reused with new specimens.

layer only one molecule in thickness. There is no way of actually determining whether these amounts represent monolayers, because the exact composition of the deposited material is unknown. The radiochemical analyses were so sensitive that they permitted accurate measurement of the amounts of film on the cathodes of the test cells even though the presence of these films could not be detected visually.

It is evident that similar curves were obtained for the first 80 hr of the two

runs depicted in Fig. 3. After that there was a significant increase in the rate of deposit in the run represented by Curve B. All of the specimens used in the two runs were prepared at the same time and under identical conditions. Therefore, it was concluded that the difference in the rates of deposit in the last hours of the runs was probably due to differences in the corrosive waters rather than in the character of the specimens. Analyses of the corrosive waters at the conclusion of the two runs revealed no significant difference in their chemical composition, with the exception of iron concentration. In the water from the run represented by Curve B, there was 0.06 ppm of iron in solution, as opposed to an iron concentration of 0.03 ppm in the Curve A water.

A second set of fresh specimens was placed in the specimen holders, and the runs were repeated, in part, using the same waters that had been employed for the two runs in Fig. 3. Curves A and B in Fig. 4 correspond, respectively, to the runs made reusing the waters from the runs of Curves A and B of Fig. 3.

It can be seen that the reuse of the corrosive waters resulted in much higher rates of deposition of metaphosphate on the cathodes, and a greater total deposit was obtained. The presence of a film on the cathodes in these runs could be detected visually through the formation of interference colors on the specimens. It was evident that the inhibitory action of the metaphosphate was exerted more rapidly in the second runs, as there were no visible deposits of corrosion products on the anodes, even in the early hours of the runs. In the preceding runs, the anodes

had been heavily coated with corrosion products.

The only detectable difference in the conditions under which the first and second sets of runs were made was the presence of corrosion products in solution at the beginning of the second set of runs. Therefore, it was concluded that these corrosion products might have been responsible for the higher rates of deposition in the runs of Fig. 4. In that event, the protective films formed on the cathodes must have been composed of metaphosphate, corrosion products, and possibly other chemicals in solution in the water. Thus, the amount of metaphosphate deposit would not present a true picture of the amount of film present on an electrode, because the metaphosphate would be only one constituent of the film.

#### Galvanic-Current Studies

The differences between the curves in Fig. 3 and those in Fig. 4 indicated a possibility that corrosion products in the water might exert a significant effect on the action of metaphosphate. The next step in this investigation, then, was to determine the effect, if any, of corrosion products in solution on the inhibitory action of metaphosphate glass, as measured by the current flow in galvanic cells.

In addition to the equipment described previously, a "zero resistance" ammeter (8) was used in these studies. This device permitted the measurement of short-circuit currents between the electrodes of the galvanic cells. This procedure was necessary because a microammeter in the circuit between the electrodes, even though of low resistance, could have a serious effect on the total current flow in the

galvanic cell. In order to measure the galvanic current between the electrodes in each of the couples, the wire that normally short-circuited the cell was disconnected. The two electrodes were then connected to the zero resistance ammeter, and the short-circuit current was determined. The cells were short-circuited again immediately after measuring the current flow.

In the first pair of runs, with the two continuous-flow systems operated in parallel, 0.5 ppm of iron powder was added to the water in System 1, and no iron was added to System 2. In a second pair of parallel runs, 0.5 ppm of iron powder was added to the water in System 2, and none to System 1. This procedure was followed in order to eliminate any possible variations in the operating characteristics of the two separate systems. By adding the iron in the form of powder, it subsequently entered solution in the same manner as when entering from the face of a corroding metal. The iron and 50 ppm of metaphosphate were added to the synthetic tap water 24 hr before beginning the runs.

Each of the curves in Fig. 5 represents the average of the results of two corresponding runs made in the two continuous-flow systems. The curves for the individual runs, obtained by averaging the current flow measurements from the several galvanic cells in each system, showed the same trends as the average curves presented in Fig. 5.

These curves reveal that the addition of iron powder to the corrosive water had a beneficial effect on the inhibitory action of the metaphosphate. It is significant that, toward the end of the runs, the curve representing the current flow in the systems with no iron added tends to approach the curve for

the systems with iron. An explanation is that continued corrosion of the specimens resulted in the further addition of corrosion products to the solution. Separate studies were conducted to determine the effects of metaphosphate and corrosion products on anode and cathode potentials and polarization in galvanic cells (11). From these studies, it was possible to show that the beneficial effect of corrosion products was due to increased polarization of the cathodes of the corrosion cells.

In the light of the film deposition, current flow, and polarization studies,

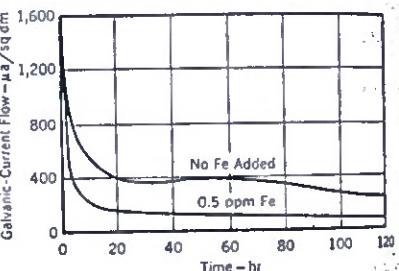


Fig. 5. Effect of Iron on Galvanic-Current Flow Inhibition by Metaphosphate

The solutions contained 50 ppm ( $\text{NaPO}_3$ ). Iron was added in powder form.

it may be concluded that corrosion products in solution have a beneficial effect on the inhibitory action of metaphosphate glasses—an effect which may be attributed to increased deposition of metaphosphate on the cathode and a resulting increase in the degree of polarization of this electrode.

#### Theory of Mechanism

It is the purpose of this section to develop a reasonable hypothesis concerning the mechanism by which meta-

May 1954

phosphates inhibit the corrosion of iron in water. This hypothesis will be based on the results obtained in the research described above, taking into account the known characteristics of metaphosphates, as determined by past investigators.

Metaphosphate has been classified as an anodic inhibitor (5, 12, 13) and as a cathodic inhibitor (2-4, 14). Through polarization studies, it has been possible to show that the inhibitor may be made to act in either manner in short-term laboratory tests (11). The results indicated that the mode of action of the inhibitor was affected greatly by the presence of corrosion products in solution, and it was concluded that metaphosphate should be classed as a cathodic inhibitor under practical operating conditions.

Metaphosphate glasses of the type employed in these studies form negatively charged particles when placed in solution in distilled water. Heavy deposits of metaphosphate were observed on the anodes in the course of the studies reported above. The presence of these deposits can probably be attributed to the dual effects of electrical attraction of the negatively charged metaphosphate to the anodic areas and subsequent adsorption or reaction between metaphosphate and the corrosion products on the metal.

Hatch (4) has suggested that electrodeposition is involved in the formation of the cathode film. It is evident that some of the metaphosphate in solution must form positively charged complex ions or colloids before electrical attraction to the cathodes takes place. The presence of trivalent cations in solution would favor the formation of these particles. It has been shown that corrosion products exert a significant

effect on the amount of metaphosphate deposited on the cathode.

Hazel (15) has demonstrated that hydrous ferric oxide and sodium metaphosphate glass may form stable positive or negative sols, or they may coagulate, depending upon the relative amounts of the reacting substances in solution. The data indicated that the formation of positively charged colloidal particles was favored by reduction in pH and increase in the iron oxide-metaphosphate ratio. During the present investigation, qualitatively similar results were obtained with metaphosphate dosages of 4-50 ppm and iron concentrations of 1-50 ppm (16). It is well known that metaphosphate will remove corrosion products from iron. At the anode, where this reaction takes place, the ratio of ferric oxide to metaphosphate is high, and the pH of the solution is at a minimum. Both of these conditions favor the formation of positively charged colloidal particles.

Consideration of the results obtained in this research, together with those obtained by past investigators, has led to the development of the following hypothesis concerning the possible mechanism of corrosion inhibition by metaphosphate glasses: Metaphosphate in solution reacts with the corrosion products in the vicinity of the anodes, resulting in the formation of positively charged colloidal particles. These particles, containing iron oxides and metaphosphate, are subsequently deposited on the cathodes through electrodeposition. The film thus formed decreases the rate of corrosion of iron in water by increasing the degree of polarization of the cathodes in the corrosion cells.

The studies in the latter phase of this research project were conducted with

the objective of determining whether the preceding hypothesis could be substantiated by experimental observations.

#### Effect of pH on Film Deposition

It has been pointed out that the electrodeposition of a cathode film must depend upon the formation of positively charged particles. It has been shown

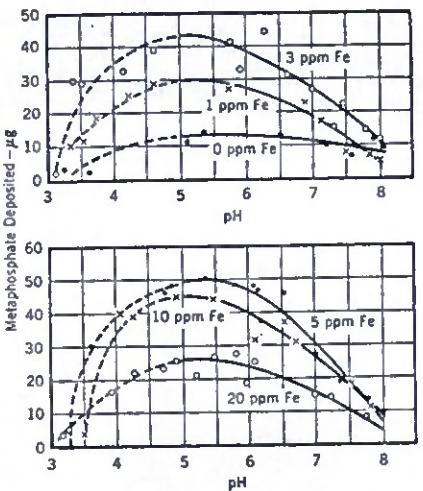


Fig. 6. Effect of pH on Metaphosphate Deposition

Test conditions: 50 ppm ( $NaPO_4$ ); pH adjusted with  $HCl$ ; current flow, 1 ma; platinum cathode; iron added as  $FeCl_3$ ; length of test, 1½ hr.

that iron and metaphosphate are capable of forming colloidal particles in tap water (15, 16). The experiments in this section were undertaken for the purpose of investigating the effect of solution pH on the deposition of metaphosphate on the cathode.

The basic equipment used in these tests consisted of a container made

of U-shaped lucite sections, fastened together by means of bolts passing through the entire unit. To eliminate contamination of the test solutions through corrosion of the electrodes, they were made of platinum. A sheet of platinum, which served as the anode, was placed between the lucite sections at one end of the unit. Platinum-covered stainless steel, turned to 0.900-in. diameter and 0.25-in. thickness to fit the available counting equipment, served as the cathode. The latter was screwed to a brass holder, and all metallic surfaces, except for the platinum, were waterproofed.

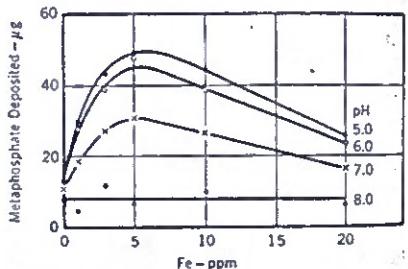


Fig. 7. Effect of Iron Concentration on Metaphosphate Deposition

Test conditions were as in Fig. 6.

Radioactive metaphosphate glass to make 50 ppm was added to 500 ml of synthetic tap water, and the pH of the solution was adjusted roughly with hydrochloric acid. The desired amount of iron was then added to the solution in the form of ferrous chloride. After 30 min of aeration the exact pH of the solution was measured, and a 180-ml sample was placed in the lucite container. This water was agitated by a laboratory stirring machine operated at a uniform speed. A constant current of 1 ma was passed

May 1954

CORROSION INHIBITION

455

between the electrodes. One-milliliter samples of the test water were evaporated and counted in triplicate, to determine the number of counts per second per milligram of metaphosphate. At the end of 1½ hr the cathode assembly was taken from the unit and rinsed slightly in distilled water to remove any radioactive test solution adhering to the metal. The cathode was then separated from the brass holder, placed in a counting cup, and counted three times. The amount of metaphosphate on the cathode was determined by the radiochemical techniques previously outlined.

In Fig. 6, the results have been presented in two groups of curves for the sake of clarity. It will be noted that, in the absence of iron, the pH of the solution, at values greater than 5.0, had very little effect on the amount of metaphosphate deposited on the cathode. The decrease in the amount of deposit at lower pH values cannot be explained satisfactorily at this time. In all solutions containing iron, the amount of deposit increased with a decrease in pH to approximately 5.0. The decrease in the amount of deposit at pH values less than 5.0 can possibly be attributed to the increasing solubility of iron. Decreasing the pH below 3.5 appeared to eliminate formation of colloidal particles, as indicated by the absence of Tyndall cones in these solutions.

Colloidal particles of iron and metaphosphate may carry net positive or negative charges. It has been well established by many investigators that the formation of a positive sol is favored by reduction in the pH of the solution. The curves in Fig. 6 show that the deposition of metaphosphate on the cathode is favored by reduction

in the pH of the solution to a value of approximately 5.0. Therefore, these results are compatible with the hypothesis that the cathode film may be formed through the deposition of positively charged colloidal particles on this electrode.

#### Effect of Iron on Film Deposition

The curves in Fig. 7, plotted from data in Fig. 6, reveal that the addition of iron to the test water had a significant effect on the amounts of metaphosphate deposited on the cathodes, in 1½ hr, at pH 5.0, 6.0, and 7.0. An increase in iron concentration to approximately 5 ppm resulted in a sharp increase in the amount of deposit. This increase can be attributed to deposition of the greater number of positively charged particles on the cathodes. A subsequent increase in iron concentration resulted in a decrease in the amount of deposit, which may be attributed to one or both of the following factors: [1] increased ferric oxide-metaphosphate ratio in the particles, resulting in a decrease in the quantity of metaphosphate deposited; and [2] increased size of the particles, resulting in a lower migration velocity in an electrical field.

It will be noted that the increase in iron concentration had little or no effect on the amount of metaphosphate deposited at a pH of 8.0. The formation of positively charged colloidal particles is inhibited by a rise in pH. Therefore, it may be concluded that, at this pH, the hydrous ferric oxide and metaphosphate did not combine to form a significant number of positively charged particles. On the other hand, in the earlier phases of this investigation (Fig. 3 and 4), it was found that the addition of small quantities of cor-

May 1954

rosion products to the solution at this pH did have a significant effect on the deposit of metaphosphate. This indicates that the removal of corrosion products by metaphosphate is more effective in producing positively charged colloidal particles than is the reaction between metaphosphate and iron added to the solution in chemical form.

The high ferric oxide-metaphosphate ratio and minimum pH in the vicinity of the anode favor the formation of colloidal particles with net positive electrostatic charges, even though conditions in the solution proper might be unfavorable to the formation of such particles. Furthermore, it has been found (17) that metaphosphate glass forms very highly hydrated particles in water. Therefore, colloidal particles containing hydrous ferric oxide and metaphosphate are probably highly hydrated. This hydration shell interferes with or retards reaction between a particle, once formed, and other particles in solution. Hence, a particle formed at the anode of a corrosion cell would have a tendency to retain its net positive charge, although conditions in the solution proper might be unfavorable to the formation or continued existence of such a particle.

The curves in Fig. 7 show that a deposit of metaphosphate was obtained on the cathode in the absence of iron. It has been found that this deposit can be attributed to the effect of calcium in solution (18).

#### Deposition of Corrosion Products in Cathode Film

It has been shown that the addition of corrosion products to the solution increases the amount of metaphosphate deposited on the cathode. It was the purpose of the experiment described in

this section to determine whether a transfer of corrosion products from anode to cathode, as postulated in the hypothesis, actually takes place.

An iron-plating bath containing ferrous chloride and calcium chloride was prepared. Approximately 75 microcuries of radioactive iron ( $Fe^{55-59}$ ) was added to this solution. Steel specimens were pickled thoroughly and placed in the plating solution. A current with a density of approximately 100 amp per square foot of specimen area was passed between the submerged specimens. After removal from the plating bath, the radioactive cathode was washed thoroughly with tap and distilled water.

This electrode was then used as the anode in an impressed-current cell. A platinum electrode, identical with those employed in preceding tests, was used as the cathode of the corrosion cell. The electrodes were immersed in 500 ml of synthetic tap water containing 50 ppm of nonradioactive metaphosphate glass, and a current of 1 ma was passed between them. The solution was agitated by means of a laboratory stirrer. A platinum electrode through which no electrical current passed served as a control specimen. The platinum electrodes were removed, rinsed in distilled water, and counted at the end of 1½ hr.

On the basis of three runs, the platinum cathode showed the presence of a significant amount of radioactive deposit at the end of the above procedure (1.33 counts per second). The control specimen, through which no electrical current passed, showed the presence of very little radioactivity above background. The only source of radioactive material in this test was the iron anode. Therefore, the presence of

radioactive deposit on the platinum cathode can only be attributed to the transfer of material from the anode to the cathode of the corrosion cell, thus substantiating the hypothesis that the cathode film contains corrosion products in addition to metaphosphate. Another inference is that it is not necessary to add iron to the water in order to cause the deposit of a cathode film containing iron. A source of this metal is made available in the corrosion process.

The presence of a relatively large deposit on the cathode in the impressed-

investigation of the effects of pH on film deposition.

A synthetic tap water solution containing 50 ppm of radioactive metaphosphate glass and 20 ppm of iron, in the form of ferrous chloride, was aerated for 30 min, and 180 ml of this water was added to each lucite container. The rate of electrical-current flow through each unit was adjusted to a desired constant value. The water was stirred continuously throughout the tests, as in the studies on the effect of pH. One-milliliter samples of the water were evaporated and counted to determine the counts per second per milligram of metaphosphate in solution. At the end of 1½ hr the platinum-faced cathodes were removed. The amount of metaphosphate deposited on each was determined by counting the specimens with the films in place. Duplicate runs were made and the results averaged for presentation in Fig. 8.

Figure 8 reveals that the rate of current flow had a marked effect on the amount of metaphosphate deposited on the cathode. Very little deposit was obtained in the absence of electrical current, and the small amount that was deposited can probably be attributed to adsorption of the chemicals on the metal. The increase in the amount of deposit with increase in current flow can be attributed to one of two factors: [1] reaction between the metaphosphate and cathodic products, causing deposition of this chemical on the cathode; or [2] electrodeposition of the metaphosphate.

To distinguish between these alternatives, it should be recalled that alkalinity is produced at the cathode, causing a rise in pH in the vicinity of this electrode (5, 8, 9). In the phase of this investigation dealing with the effects

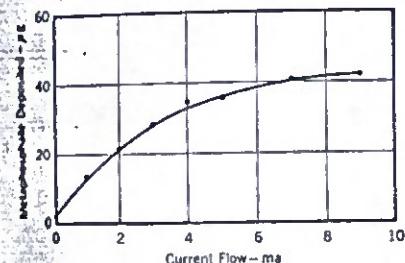


Fig. 8. Effect of Electrical-Current Flow on Metaphosphate Deposition

Test conditions: 50 ppm ( $NaPO_3$ ); 20 ppm  $Fe(FeCl_2)$ ; pH 7.7.

current cell, and a very small deposit on the control specimen, is consistent with the hypothesis that electrodeposition is the primary mechanism in the formation of the cathode film.

#### Role of Electrical-Current Flow in Film Deposition

This section of the investigation was undertaken to determine whether cathode film formation is a function of the electrical current flowing through the cell. The equipment used in these studies was identical with that in the

of pH, it was shown that a rise in pH could be expected to result in a smaller cathode deposit. From this fact, it is evident that the increase in deposit with increased current flow occurred in spite of the alkalinity formed at the cathode rather than because of it. Consequently, it must be concluded that the cathode film of metaphosphate and corrosion products is formed through electrodeposition, thus confirming a portion of the hypothesis previously outlined.

#### Evaluation

Hatch (4) has suggested the possibility that the calcium salt or complex of metaphosphate glass may form positively charged colloidal particles in solution. On the other hand, Reitemeier and Buehrer (19) concluded that colloidal particles of calcium and metaphosphate were not formed, even in supersaturated solutions of calcium carbonate. It should be pointed out, however, that this conclusion was based on the absence of a Tyndall cone in such solutions, a condition that does not necessarily preclude the possibility of a colloidal suspension.

It is well known that metaphosphate exists in the form of a negatively charged particle in distilled water. In this investigation, no significant deposit of metaphosphate was found on platinum cathodes immersed in distilled water containing metaphosphate. All migration of metaphosphate under these conditions was in the direction of the anode. In waters containing calcium, significant deposits of metaphosphate were found on the platinum cathodes (Fig. 6 and 7). Therefore, it may be concluded that calcium and metaphosphate combine to form positively charged particles. No conclusion can

be reached, however, as to whether these particles are ionic or colloidal in nature, as no Tyndall cones were observed in these samples. Previous studies (11) showed that, when metaphosphate was deposited on the cathode in the absence of iron, it had little or no effect on the polarization of this electrode. Therefore, the inhibitory action of metaphosphate glass cannot be attributed solely to this deposit.

In the film deposition studies and in the section dealing with the effect of iron on film formation, it was found that the presence of a small amount of iron in the water resulted in a significant increase in the amount of metaphosphate deposited on the cathodes. The results of the galvanic-current flow studies indicated that the addition of iron had a beneficial effect on the inhibitory action of metaphosphate. Other studies (11) have revealed that the beneficial effect was due to increased polarization of the cathodes in the presence of iron.

Metaphosphates remove corrosion products from the anodes of corrosion cells. At these locations are found the conditions of low pH and high iron concentration that are most favorable to the formation of positively charged colloidal particles of metaphosphate and hydrous ferric oxide. The study of the deposition of corrosion products in the cathode film showed that a transfer of corrosion products from anode to cathode actually took place. These results confirm the hypothesis that metaphosphate and hydrous ferric oxides are constituents of the protective film. The corrosion products removed from the anodes by metaphosphate may be considered a source of the oxide which is subsequently deposited on the cathodes in combination with the metaphosphate.

May 1954

CORROSION INHIBITION

459

The investigation has shown that the protective film is formed on the cathodes primarily through a process of electrodeposition. This conclusion is in agreement with the findings of Hatch (4) and is consistent with a theory of cathode film formation through electrodeposition of positively charged colloidal particles containing metaphosphate and hydrous ferric oxides.

It was found that a decrease in pH to approximately 5.0 resulted in an increase in cathode film deposition. A further decrease in pH resulted in a sharp decrease in film formation. It has been pointed out that these effects are consistent with the theory of colloidal action which has been developed. A decrease in pH might be expected to result in the formation of a greater number of positively charged colloidal particles (or more highly charged particles). The decrease in film formation at lower pH may be attributed to the increased solubility of iron. These results are in agreement with those of Hatch and Rice (1), who found that the inhibitory action in metaphosphate-treated water appeared to be more pronounced as the pH decreased to approximately 5.0. They also found that the inhibitory action decreased at pH values less than 5.0.

It should be pointed out that the findings of this investigation do not negate or conflict with the results obtained by most previous investigators. Rather, an explanation of the mechanism underlying their findings has been disclosed. This makes possible a direct correlation between the present findings and those of past investigators. The new information brought to light during these studies may be used to explain conflicting or incon-

sistent results reported by some investigators.

#### Conclusions

The results obtained in this research work lead to the following conclusions about the inhibitory action of metaphosphate glass on the corrosion of iron in water:

1. Metaphosphate glass, when added to solution in sufficient quantity, will remove corrosion products from the anodes of corrosion cells.
2. In the vicinity of the anodes of corrosion cells, there is a high ferric oxide-metaphosphate ratio and a minimum pH. These conditions are favorable to the formation of positively charged colloidal particles of hydrous ferric oxide and metaphosphate.
3. The rate of deposition of metaphosphate on cathodic areas, as well as its inhibitory action, is enhanced by the presence of corrosion products in solution.
4. Some of the corrosion products stripped from anodes by metaphosphate are subsequently deposited on the cathodes.
5. The protective film formed on the cathode contains colloidal particles made up of metaphosphate, ferric oxide, and other chemicals deposited from solution.
6. The protective film is deposited on the cathode through a process of electrodeposition.
7. The protective film reduces the rate of corrosion by increasing the degree of polarization of the cathode.
8. The rate of deposition of metaphosphate on cathodes is highest at a pH of 5.0 and decreases above and below this pH value.
9. The rate of deposition of metaphosphate on cathodes increases with

an increase in iron concentration in the water up to a limiting value.

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#### References

1. HATCH, G. B. & RICE, OWEN. Corrosion Control With Threshold Treatment. *Ind. Eng. Chem.*, 32:1572 (1940).
2. MANSA, J. L. & SZYBIALSKI, WACLAW. Corrosion Due to Tuberculation in Water Systems. *Acta Chem. Scand.*, pp. 1275, 1293 (1950); *Corrosion*, 8: 381, 388 (1952).
3. RAISTRICK, B. Condensed Phosphates and Corrosion Control. *Chem. & Ind.*, p. 408 (May 10, 1952).
4. HATCH, G. B. Protective Film Formation With Phosphate Glasses. *Ind. Eng. Chem.*, 44: 1775 (1952).
5. EVANS, U. R. *Metallic Corrosion: Passivity and Protection*. Edward Arnold & Co., London (1946).
6. EVANS, U. R. Corrosion Problems Arising From Water in Chemical Industry. *Chem. & Ind.*, p. 1193 (Dec. 31, 1951).
7. HATCH, G. B. & RICE, OWEN. Corrosion Control With Threshold Treatment. *Ind. Eng. Chem.*, 37:752 (1945).
8. UHLIG, H. H. *Corrosion Handbook*. John Wiley & Sons, New York (1948).
9. ELIASSEN, ROLF & LAMB, J. C., III. Mechanism of the Internal Corrosion of Water Pipe. *Jour. AWWA*, 45: 1281 (Dec. 1953).
10. ELIASSEN, ROLF, ET AL. Studies on Radioisotope Removal by Water Treatment Processes. *Jour. AWWA*, 43:615 (Aug. 1951).
11. LAMB, J. C., III & ELIASSEN, ROLF. Corrosion Control With Metaphosphate Glass. *J. NEWWA* (in press).
12. THORNHILL, R. S. Experimental Approach to the Problem of Tuberculosis by Waters. *Chem. & Ind.*, p. 1201 (Dec. 31, 1951).
13. KAHLER, H. L. & GAUGHAN, P. J. Protection of Metals Against Pitting, Tuberculosis, and General Corrosion. *Ind. Eng. Chem.*, 44:1770 (1952).
14. HATCH, G. B. Inhibition of Galvanic Attack of Steel With Phosphate Glasses. *Ind. Eng. Chem.*, 44:1780 (1952).
15. HAZEL, FRED. The Effect of Small Concentrations of Hexametaphosphate on Iron Oxide Surfaces. *J. Phys. Chem.*, 46:516 (1942).
16. LAMB, J. C., III. The Mechanism of Corrosion Inhibition by Sodium Metaphosphate Glass. Thesis, Massachusetts Inst. of Technology, Cambridge, Mass. (1953).
17. VAN WAZER, J. R. Physical Properties of Solutions of a Sodium Phosphate Glass. *Ind. Eng. Chem.*, 41:15 (1949).
18. LAMB, J. C., III & ELIASSEN, ROLF. Radioactive-Tracer Studies of Corrosion Inhibition by Metaphosphate. *J. Boston Soc. Civ. Engrs.* (in press).
19. REITEMEIER, R. F. & BUEHRER, T. F. Inhibiting Action of Minute Amounts of Sodium Hexametaphosphate on the Precipitation of Calcium Carbonate From Ammoniacal Solutions. *J. Phys. Chem.*, 44:535, 552 (1940).

## Mechanism and Control of Scale Formation in Sea Water Distillation

By W. F. Langlier

*A contribution to the Journal by W. F. Langlier, Prof. of San. Eng., Univ. of California, Berkeley, Calif.*

IN 1941, when the military services accepted engine-driven compression equipment for the distillation of sea water, serious problems in the control of evaporator scale deposits were quickly brought to light, and several investigations were initiated in an endeavor to solve these difficulties. This paper describes briefly some of the conclusions derived from a research project recently completed by the Institute of Engineering Research at the University of California, Berkeley, Calif.

The project involved extensive laboratory studies in the chemistry of evaporator deposits and also the full-scale operation of a standard 60-gph thermocompression still supplied with water from San Francisco Bay. The project was sponsored by and received the intimate cooperation of the Sanitary Engineering Branch, US Army Corps of Engineers, Fort Belvoir, Va.

No simple theory is completely adequate to explain all of the manifestations and apparent contradictions associated with scale formation in the distillation of sea waters. Just when it appears that all possible deviations from normal have been accounted for, a new and challenging situation arises to confound the investigator. With full-strength untreated sea water, a unit may operate for as long as 600 hr

between descalings, whereas, with diluted harbor water, the same unit may operate for only 200 hr. A unit that develops magnesium hydroxide scale when operated at one location on the Atlantic Ocean is found to develop calcium carbonate scale when operated at another. These and other apparent inconsistencies have been observed. A few generalizations can, however, be made:

1. The avoidance of hard sulfate scale requires that the sea water should not be concentrated to less than one-third of its original volume—that is, the concentration factor should not exceed 3.0. This is accomplished by controlling the blowdown rate so that it does not fall below 33 per cent of the rate of feed.

2. Operating as in the preceding paragraph, the scaling potential of sea water is normally a function of total alkalinity, but silica, when present in significant amounts, either as turbidity or in solution, exerts an unfavorable effect disproportionate to its concentration. Coastal and harbor waters may differ from normal sea water in these respects.

3. The dry weight of scale deposited within a given interval is roughly equivalent to the total alkalinity in the volume of water distilled. Depending