THE CONTROL OF SCALE AND CORROSION IN WATER SYSTEMS

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THESIS

This is to certify that the

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THE CONTROL OF SCALE AND
CORROSION IN WATER SYSTEMS

By

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A THESIS

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This thesis attempts a general study of the problem of controlling corrosion, scale and tuberculation in water supply systems. It covers twelve term hours of study, experimentation and preparation.

A survey of recent literature concerning this problem is briefly summarized, with especial attention to the use of sodium hexametaphosphate as a corrosion control in water systems. The use of sodium hexametaphosphate in several cities is discussed, together with results of studies reported in the literature in connection with the use of this chemical (often known as a glassy phosphate) under various condition approximating those found in a public water system.

A series of tests with sodium hexametaphosphate and other chemicals used in corrosion control is reported and results discussed. In general these experiments are tests to determine the effect of dissolved oxygen, pH, and various additions of Calgon (commercial name for sodium hexametaphosphate) upon the rates at which steel bars corrode. These tests are described in some detail, but mainly consisted of preparing various waters for test, and rotating steel rods in these waters in such a way as to prevent the entrance of any additional supply of oxygen.

An unpublished series of tests By Professor Edward F. Eldridge of Michigan State College Engineering Experiment

Station, studying the value of sodium hexametaphosphate as a means of inhibiting corrosion, has been used as a basis for these tests. The tests reported, however, are almost entirely original upon the part of the author, and do not follow the tests made by Professor Eldridge, except in a general way.

Finally, a series of tests to determine the effect of sodium hexametaphosphate upon the softening and iron removing capacity of a zeolite softener are described and discussed.

DEFINITION OF TERMS

The terminology used in this paper will be that adopted by the Committee on Water Conditioning Methods to Inhibit Corrosion which reported to the American Water Works Association of June 24, 1942.

"The term CORROSION is restricted to mean the removal of metal from an exposed surface regardless of it's subsequent fate. Where the metal removed becomes encrusted on the pipe as an insoluble oxide or other compound, the terms TUBERCULATION or INCRUSTATION are used. RED WATER refers to the presence of suspended iron compounds in the water, and may be due to corrosion or to the fact that the water itself contains iron. PITTING refers to the localization of corrosion in small, well-defined areas of penetration."

THE PROBLEM OF WATER PIPE CORROSION

All types of waters are corrosive to a greater or lesser extent. Some waters are so aggressive due to the presence of certain minerals and gasses that definite measures must be taken to protect conduits carrying these waters, else there will be extensive damage to the metal of the conduits and great nuisance to the consumers of the water. Waters found in most water systems are only slightly aggressive, yet even these are corrosive enough to slowly and steadily damage pipe lines, storage tanks, heaters and other parts of water systems. In addition, most water systems tend to build up blankets of iron oxide and hydroxide which will on occasion break loose and harass housewives and other users with epidemics of "red water". Pipe corrosion, therefore, from this view alone is a serious enough problem to warrant extensive investigation, for unexpected surges of iron oxide deposit often causes extensive damage to laundry, household fixtures and other utilities. "Red water" nuisance always causes complaint and tends toward dissatisfaction with a water supply management.

From an economic viewpoint an even more costly and damaging result of corrosion is the restriction and even stoppage of pipe lines by the tubercles of corrosion.

These tubercles are particles of the pipe conduit, $\frac{1}{4}$ to 1 inch long, which have broken loose due to corrosion. In time these tubercles tend to almost fill portions of water pipes, increasing friction and reducing carrying capacity to a fraction of the original value. Removal of these restrictions is expensive and difficult, and at best a temporary measure. Pipe lines must sometimes be replaced if tuberculation becomes excessive, and even partial restriction of pipe areas causes great expense due to reduced capacity and increased power costs.

The corrosive action of water is greatly increased by increased temperatures. Storage tanks, piping and heaters connected with hot water systems are subject to damage far more than cold water pipes, and often are eaten out and damaged beyond repair in a fraction of their otherwise useful lives.

As yet, little progress has been made in reaching any complete solution of the problem. The following methods have in some cases inhibited corrosion:

1. Galvanized coatings. Zink galvanizing is sometimes successful, yet may be attacked by some waters as readily as the metal coated. Coatings of metals other than zink may prove resitant to the more aggressive waters, and therefore useful for iron pipes, but little data of this nature is at present available.

2. Coating of paint, cement and other water-proof materials. Various coatings have been used, some with considerable success. Some of the most successful materials have proved to impart a very bad taste and are therefore objectionable. The most common and successful coating material is a cement-sand mixture. Any coatings thus far developed have been difficult to place and maintain during laying of the pipe, and are sometimes disturbed. A "localized" corrosion results. No coating material has proved useful in hot water lines.

3. Treating to raise the pH of the water, laying down of a calcium carbonate scale on the inside surface of the pipe and removal of carbon dioxide from the water. These three means of protecting pipe lines are secured by treating to obtain a positive stability index, usually with lime or some other hydroxide. This method of protecting pipe lines is that in most common favor at the present time. Although one of the best and most popular methods of controlling corrosion, the calcium carbonate scale is very soft and portions tend to break away, leaving the pipe exposed. In some instances this method has been of little or no help at all. In particular it is very unsatisfactory in hot water systems.

4. The use of polyphosphates and silicates to pro-

duce protective films on the interior of pipe lines. These chemicals have in some instances proved very successful, and in other instances have proved unsuccessful. Experimental data is not yet available on proper dosage and other factors necessary to produce satisfactory protective films. Polyphosphates, in particular, are one of the most promising methods of attacking the corrosive problem. This paper will discuss sodium hexametaphosphate (a polyphosphate) commercially known as Calgon, a chemical which is coming into extensive use as an agent for inhibiting corrosion.

5. Removal of oxygen. Oxygen is the most active agent in causing aggressive waters. No completely successful method of removing oxygen in large quantities has been developed. Vacuum, followed by sodium sulphate, heat or scrap metal has been used experimentally.

6. Cathodic protection. Cathodic protection consists of creating a slightly negative potential in the metal which is sufficient to prevent the formation of positive Fe ions. This method is used extensively in connection with the protection of water tanks. No successful means of cathodic protection for water pipe lines has been developed.

7. Asbestos cement pipe and other conduits which are not subject to corrosion. Asbestos cement pipe, brass

piping in homes and glass tube hot water heaters are promising new developments which promise to help eliminate much of the "red water" problem of domestic and possibly some commercial systems. Asbestos cement pipe is coming into wide usage in the United States at the present time, but has not yet won the full confidence of practicing engineers. Asbestos cement pipe does not have the strength of cast iron pipe. Glass tube hot water heaters are a very recent development.

Theory of the Chemistry of Corrosion

The most common explanation of the corrosion of the interior metal of pipe lines is the electro-chemical reaction theory. The reaction takes place in small areas due to slight differences of metal structure and of the water in contact with the metal. Using iron, the most common example, we have the following chemical explanation:

$H_2O = H^+ + OH^-$ (water dissociates)

Fe (dissolving) $= Fe^{++} +$ 2 electrons

$2H^+ +$ 2 electrons $= 2H$ (Atomic hydrogen)

The hydrogen combines with the dissolved oxygen in the water as follows:

$$4H + O_2 = 2H_2O$$

Iron ions form ferrous hydroxide, which is one form of iron rust:

$Fe^{++} + 2OH^- = Fe(OH)_2$

$Fe(OH)_2 + O_2$ (dissolved oxygen) $= Fe(OH)_3$

It is obvious that the presence of dissolved oxygen in water is the most active agent for causing pipe corro-

sion and that corrosion is not noticeably present except in the presence of dissolved oxygen.

Carbon dioxide is also an active agent of corrosion. Carbon dioxide combines with water to form carbonic acid, which in turn dissociates into hydrogen ions. This increase in the number of hydrogen ions, in turn increasing the rate at which iron is dissolved into the water. An inspection of the chemical equations of corrosion indicates that ionic hydrogen is necessary for a rapid rate of corrosion.

Carbon dioxide also has the effect of dissolving protective coatings of rust and other scale, leaving the pipe walls clean and easily accessible to the dissolved oxygen in the water.

The rate at which pipe lines corrode is greatly dependent upon the purity of the iron of the pipe. Pure iron does not corrode, but cast iron pipe is never pure iron, but rather made up of iron of varying degrees of purity. The relation between corrosion and impurities of the metal of cast iron pipes is well explained by Babbitt and Doland as follows:

"The corrosion of the metal (of the pipe) is the result of setting up an electro-chemical action between two dissimilar metals, or between minute impurities in a metal that bear a different electric potential toward each other.

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"The corrosion of the metal (of the pipe) is the result of setting up an electro-chemical action between two dissimilar metals, or between minute impurities in a metal that bear a different electric potential toward each other.

An electric current is set up between the two dissimilar metals, and it continues to flow until the electrolyte is neutralized or the electrodes are changed into substances of the same electric potential. Under normal conditions in nature the electrolyte between the two metals is continuously renewed, so that the corrosion of the anode is continuous unless other conditions set in to interrupt the current. The rapidity of corrosion is dependent on the difference of potential between the parts of the metal and on the strength of the electrolyte to neutralize the electric charges delivered to it.

"The rusting of iron and steel can be explained by this hypothesis. Iron rust is a hydrated oxide of iron ($Fe_2 O_3, nH_2O$). It will form only in the presence of iron, oxygen and water. The absence of any one of these will preclude the formation of rust. The oxygen dissolved in the water and the water itself form a weak electrolyte solution. Now if pure iron is introduced into the water, experiment has demonstrated that it will not rust. Ordinary wrought iron and steel contain many impurities. The less homogeneous the composition of the metal the greater the difference of electric potential between spots on the surface and, hence the more rapid the formation of rust or the corrosion of the metal.

"Among the principal factors to effect corrosion of metals may be included: electrode potential; overvoltage of metal; protective-film formation by the metal itself; homogeniety of the metal, both chemical and physical; the kinds of metals involved; the electrolyte; the temperature; protective-film; turbulence in the solution; oxygen concentration in the solution; ionic concentration in the electrolyte, particularly hydrogen-ion concentration; and electrolysis. The relative importance of the various factors causing corrosion varies with the environment involved; but, in general, electrode potential, overvoltage, hydrogenion concentration or pH, and oxygen concentration are always important.

"Oxygen plays an important part in corrosion because when metal goes into electrolytic solution nascent hydrogen is formed, which reacts with the oxygen, removing the protective film of hydrogen, exposing more metalix surface for the formation of hydrogen, with resultant corrosion of the metal."

THE USE OF SODIUM HEXAMETAPHOSPHATE IN CORROSION CONTROL

"The soluble Meta- and pyrophisphates possess certain properties which are unusual. The complex phosphate ions produced by these substances are capable of taking up such ions as calcium, iron and others which might be precipitated under conditions prevailing in the water, and of holding them in the form of a soluble complex ion" - E.W. Moore, Associate Professor of Sanitary Chemistry, Harvard Graduate School of Engineering and Chairman of the American Water Works Association Committee on Water Conditioning Methods to Inhibit Corrosion.

The use of sodium hexametaphosphate in controlling corrosion is a very recent development, not over ten years old. Probably the first uses of this chemical as a corrosion inhibitor were in Columbus, Ohio, Dallas, Texas and Hempstead Long Island.

For years the ability of sodium meta-and pyrophosphates to hold up ions of calcium and iron has been recognized. Calgon, a phosphate glass, was first used in water works practice in Columbus, Ohio for the purpose of reducing the amount of recarbonation necessary after lime-soda softening, so that the pH of the water could be raised for the purpose of inhibiting corrosion. The phosphate glass proved successful for this purpose, the pH was successfully raised, and "red water" conditions were much improved by the treatment, particularly in hot water tanks.

Following the successful use of the chemical at Columbus, its use was begun at Dallas, Texas, where a reduction of "red water" was obtained by the use of glassy phosphate alone, combined with a slow lowering instead of raising of the pH.

At about the same time that the phosphate treatment was begun in Dallas its use was also started at Hemstead, Long Island in the expectation of improving "red water" conditions by raising pH. "Red water difficulties were eliminated within a short period of time, but further tests indicated that the high pH (9.2-9.4) was not necessary for successful elimination of "red water" troubles, and equally good results were obtained with pH of about 7.0.

Trials by the nearby cities of Garden City, Long Island and Fairhaven, Massachusetts, showed without question, that satisfactory results could be obtained with these waters with glassy phosphates at pH 6.2 and 5.4 respectively and that the phosphate itself was capable of greatly improving "red water" conditions.

These successful uses of phosphate in water supply systems encouraged further tests, both in the field and laboratory. Experimentation indicated that glassy phosphates were capable of decreasing corrosion in iron and

other pipes by adsorbing the phosphates on the metallic surfaces (probably as phosphates of the metals) and by holding up ions of iron which would otherwise precipitates as iron hydroxide (rust).

Although considerable laboratory data have been gathered in connection with the use of metaphosphates in water systems, the best results have been obtained in actual application to water systems. The reason for this seems to be that the metaphosphates require considerable volume and velocity of flow, and that this volume and velocity (which is often lacking in laboratory tests) is as important to good results as the concentration of the chemical.

One of the most interesting experiments carried on with metaphosphates was that of E. Mood of the New Haven, Connecticut Water Company. Mood fed New Haven water (A soft, mildy aggressive water with pH of 6.6-6.8 and iron content of 0.05 ppm) through 45 foot lengths of 3/4 inch black iron pipe connected to a constant level box. He passed untreated water through all three pipes. Iron determinations were made at various intervals of time and showed that the iron content of the untreated water increased 8 fold to an average of 0.41 ppm. Treatment with 0.11 ppm of metaphosphate held the iron content to 0.11 ppm average, or twice that of the raw supply. Treatment with 0.33 ppm prevented any apparent increase in the iron

content of the water after it entered the pipe. Soft marble slabs were placed under the discharge of the treated water for 72 hours without any signs of staining.

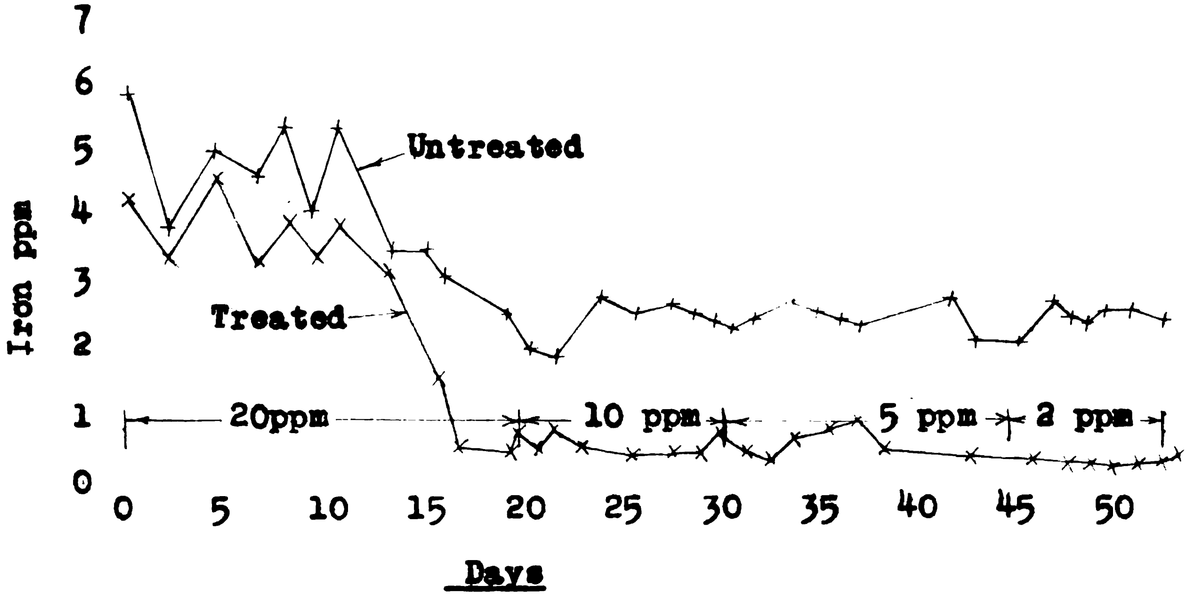
Mood also studied the effect of metaphosphate treatment on loss of flow in 3/4 inch black iron pipe. His experiments indicated that this treatment reduces, but does not eliminate loss of flow due to tubercle formation. After 27 days test untreated water showed a reduction of flow of 41.7%, 0.11 ppm treated water showed a reduction of flow of 19.3% and 0.33 ppm treated water showed a reduction of 15.5%

Evans and Shuey, of the Cincinnati, Ohio Water Company, experimented with tap water, allowing flow under constant head an an initial rate of 3 gallons per minute through two 20 foot lengths of ½-inch black iron pipe, 4 ppm of metaphosphate being applied to water passing through one pipe. Results are tabluated on the following sheet.

	Metaphosphate Treated	Untreated
Initial flow (gpm)	3	3
Decrease in flow (gpm)	0.31	1.54
Decrease in flow (%)	10	51
Increase in loss of head (inches)	37.25	78.13
Hazen Williams C at start	111	111
Hazen Williams C at end	65	27

Results of Flow Tests on Untreated and Metaphosphate-Treated Tap Water After 78 Days Run at Cincinnati,Ohio

Also of interest and deemed worth of reproduction is a plotting by Mr. H.P. Stockwell, Jr., Chemical Engineer for the Ottawa, Ontario Water Purification Plant, showing the effect of metaphosphate treatment on iron content of water passing through new wrought-iron pipe.



Effect of Metaphosphate Treatment on Iron Content of Water Passing Through New Wrought-Iron Pipe

While most data of field use of the glassy phosphates are of a favorable nature, many conflicting results have been reported which seem to indicate that the chemical is not successful as a corrosion inhibitor in all cases. Some very reliable engineers and chemists are of the belief that the phosphates do not have any value as corrosion inhibitors. For instance, Frank E. Hale, Director of Laboratories, Department of Water Supply, Gas and Electricity, New York City, is of the opinion that hexametaphosphate is corrosive, and that reported improvement of "red water" conditions are due to the ability of the phosphates to hold iron in solution rather than any ability to inhibit corrosion. Because of his strong beliefs he has not permitted the use of the phosphates in New York City, fearing damage might result to the cities' buildings. A few other well recognized men in the waterworks field seem to agree with Hale, However,the general concensus of opinion seems contrary to that of Mr. Hale, and much evidence has been gathered to substantiate the opinion that the phosphates do have great value. Indeed, many adverse reports seem to be based upon inconclusive data or experiments under conditions which do not measure the phosphates' true value.

Already mentioned in this connection is the necessity for a large volume of flow in pipe lines to obtain a good coating of iron phosphate protection on the inside of the

water pipes. Tests indicate that two or three parts per million concentration with continued passage of water through pipe lines is of more value than a concentration ten times as strong under stagnant or low flow conditions. In fact recent studies indicate that hexametaphosphate is of only slight value unless accompanied by a considerable volume and velocity of flow. However, once a satisfactory film is formed, stagnant or low flow conditions no longer seem to affect the efficiencies of the phosphates.

For this reason it is usually recommended that an initial feed of five or more parts per million be used for a period of several weeks, followed by a slow reduction to one or two parts per million. It is of course most important that the initial heavy concentrations of hexametaphosphate be accompanied by as high a volume and velocity of flow as possible.

Tests also indicate that the usual concentration of one or two parts per million of glassy phosphate do not inhibit corrosion of hot water systems, though they probably do reduce the rate of corrosion. It is well recognized that hot water is several times as corrosive as cold water and therefore is much more difficult to control. A commercial form of sodium hexametaphosphate known as Micromet has proved very helpful in inhibiting

corrosion in hot water lines. Micromet is a glass which dissolves at a rate of about 0.8% of its weight per day. If placed in the cold water inlet line so as to supply about 25 parts per million concentration to the water a considerable reduction in the rate of corrosion is observed. Reports indicate that glassy phosphates in a strength of 25 parts per million will completely inhibit corrosion in many hot water lines.

Studies of corrosion show that the rate of corrosion normally increases with an increased rate of flow. The corrosion of iron results in the formation of a protective film of hydrogen gas on the pipe interiors, but this film is swept away by the movement of rapidly flowing water. The large volume of water flowing provides an ample supply of oxygen, and corrosion is very rapid. However, studies by Owen Rice of Calgon, Inc., and others have indicated that high rates of flow decrease instead of increase the rate of corrosion if as much as one part per million of sodium hexametaphosphate is added to the water.

In this connection, studies by Rice with 40 foot lengths of black iron pipe are of interest. Rice studied head losses in the pipes during 28 days of time, reporting results obtained with pipes through which water with concentrations of zero to five parts per million of

phosphate was passed. His results indicate that in this particular test, five parts per million of phosphate reduced the head loss due to formation of tubercles to one sixth of that obtained with raw water.

These experiments by Rice show that water of low pH corrode pipes in a uniform manner with little tuberculation. As the pH increases corrosion becomes more localized and the result is formation of tubercles rather than a uniform corrosion. If metaphosphate is added, this same condition holds, except that tubercles are smaller in number and size, darker in color and more dense.

When a test similar to that just described with 40 foot lengths of black iron pipe was performed to study the effect of pH on head loss due to tuberculation, results indicated that treated and untreated water showed a head loss rise over ten times as high at pH 7.5 as at pH 5.0. A concentration of 5 parts per million of metaphosphate helped reduce rise in head loss in pipes exposed to water with both high and low pH. The test shows that high pH, although greatly reducing rate of corrosion, does increase head losses in pipes due to formation of tubercles.

It would seem that metaphosphate treated waters give best results with low pH because of the ability of phosphates to give protection against corrosion, a protection

that heretofore could be obtained only by raising pH. These lower ph's reduce tuberculation, and therefore reduce pipe head loss. This procedure of reducing pH is contrary to standard water works practice, but is the method recommended by operators who have used hexametaphosphate with success.

The matter of reducing the pH of water from standard values of 8.5 or 9.0 to around 6.0 or 6.5 is not without problems in itself. A quick reduction in pH will cause an epidemic of "red water" with accompanying dissatisfaction and complaints. Since metaphosphate has the effect of lowering pH, its use requires a careful regulation of pH during the first few weeks of use. pH is most successfully lowered by very small incrments to the desired value. Even these small increments of reduction are often accompanied with a breaking loose of rust crusts and a very rusty water. If an adequate plan of flushing accompanies the reduction of pH, little if any difficulties will result.

Although the reduction of corrosion and tuberculation are of great importance, the prevention of precipitation of calcium carbonate scale and the prevention of "red water" due to precipitation of dissolved iron from well water (after oxidation) are equally vital to good water works operation.

Good"customer relations" and maintenance of resonable

pipe head losses are usually dependent upon preventing scales of rust and calcium carbonate from forming on the inside of pipe lines. Such precipitations cause roughness on the inside of the pipes, reduce the area available for carrying water and often break loose at intervals to cause "red water".

While there may be some questions as to the ability of the metaphosphates to inhibit corrosion, there is no question as to the ability of the chemical to hold calcium and iron in a complex ion. In the past, most water supply people have preferred to have a certain amount of precipitation of calcium carbonate upon the interiors of pipe lines to prevent corrosion. But if such protection can be obtained with a phosphate-iron protective scale on the pipe interior these calcium carbonate scales are undesirable since they increase head loss, decrease carrying capacity, and tend to clog water meters and valves. Calcium carbonate scale in hot water coils is most undesirable since such scale reduces the ability of the coil to conduct heat.

Water treated by the lime-soda method tends to form heavy deposits of calcium carbonate scale because the treatment precipitates calcium carbonate and recarbonation often fails to change all suspended carbonates into bicarbonates. Many such plants are now using metaphosphates to hold the calcium carbonate in suspension, and to avoid calcium carbonate growth upon the grains of filter sand. For instance, the Lansing, Michigan lime-soda treatment plant adds 0.25 parts per million of Nalco-519 (a metaphosphate manufactured by the National Aluminate Corporation) just before filtration and 0.25 parts per million of Nalco-519 after filtration.

More interesting yet is the ability of small amounts of metaphosphates to prevent the precipitation of dissolved iron from well water. Well water often contains appreciable quantities of dissolved iron and usually is devoid of oxygen. When such water is aerated in reservoirs and storage tanks oxygen is absorbed, causing the ferrous iron to be oxidized to a ferric iron, which is a form or rust.

Rust so formed often precipitates in water mains and causes "red water" after a rise of fall in pH or other change in the normal chemical condition of the water. Any water with over 0.3 parts per million of iron is generally considered to be of questionable value as a public water supply. Water far below this value in iron content can form rust scale upon the interiors of pipe mains and seriously harass the water supply management with "red water" problems.

The addition of one part per million of sodium hexa-

metaphosphate for each part per million of iron (as Fe), if added before chlorination and before the water has an opportunity to absorb oxygen will prevent the precipitation of dissolved iron. Once the iron is held in a complex ion by the phosphate the iron will be carried completely through the distribution system.

After prolonged contact of the water with air the iron will oxidize, but 2 parts per million of iron is not noticeable when oxidized and an iron content below 5 parts per million is not particularly objectionable, though there may be some taste. If as much as four times as much metaphosphate as iron is present in the water, the iron will not be oxidized, even if exposed to a very high oxygen content in the water after the metaphosphate is added.

The ability of metaphosphates to hold iron in solution has been strikingly demonstrated to this writer by observation of the results of tests with iron rods, described in this paper. In all cases, it was observed that tests which badly discolored untreated waters did not cause any particular discoloration of waters containing twelve or more parts per million of Calgon. Since in many of these tests the loss of iron by the rods exposed to Calgon treated waters was as high as the loss in untreated waters it must be concluded that heavy concentrations of iron

were held in suspension in the treated waters by the action of phosphate ions.

When metaphosphates are dissolved in water the phosphorous pentoxide P_2O_5 combines with water to form metaphosphoric acid or pyrophosphoric acid thus:

$P_2O_5 + H_2O = 2\ HPO_3$ (Metaphosphoric Acid)

$P_2O_5 + 2\ H_2O = H_4P_2O_7$ (Pyrophosphoric Acid)

Both metaphosphoric acid and pyrophosphoric acid are capable of holding iron and calcium in suspension. The two acids are in almost every way similar.

Metaphorphoric acid and pyrophosphoric acid both slowly hydrolize to orthophosphoric acid, which has no value, as an inhibitor of corrosion.

Metaphosphates are usually fed by dissolving the phosphate glass in solution. Because of the tendency to hydrolize to an orthophosphate it is well to make up a fresh solution every ten days. Most metaphosphates are shipped in broken glass in 100 pound waterproof bags. Not over three months supply should be on hand at one time because the glass tends to become covered with a film of reverted phosphate if stored under moist conditions. The addition of soda ash in small quantities helps keep strong solutions in a metaphosphate form for a longer time than is otherwise possible.

Metaphospates are a true glass and have no limiting solubility. However it is recommended that a maximum feed solution of one pound per gallon be used, because more concentrated solutions become too viscous to handle. The usual feed solution used varies from one part per hundred to one part per thousand concentration. The solution is usually fed by a force feeding arrangement of the type usually used for adding chemical solutions to water supplies.

High concentrations of metaphosphate are highly corrosive to metal. Wood or concrete tanks are best for holding the concentrated feed solution.

An exhaustive study of the physiology of sodium hexametaphospahte by K.K. Jones, Assistant Professor of Physiology and Pharmacology, Northwestern Medical School, has led to the conclusion that the metaphosphates are relatively non-toxic when taken by mouth, and can cause no toxic or other undesirable effects in concentrations which might be used in water supply systems. Orthophosphates are considerably more toxic than pyrophosphates. However, it is estimated that a concentration of orthophosphate fifty times higher than would ever be used in a water distribution system would be required to produce an even slightly toxic effect. Feeding very heavy doses of metaphosphate to rats and rabbits over long periods of time produced no

unpleasant results other than temporary cases of diarrhea.

Metaphosphates have no effect upon sofening or iron removing capacity of zeolite softeners. A series of experiments reported in this paper show no difference in results with treated and untreated water. It is interesting to note that hexametaphosphate is a sequestering or softening agent in itself and capable of softening water. It is often used for this purpose in households and laundries. However, the very small additions of phosphates used for scale and corrosion control are too minute to have any sofetning effect.

The cost of adding sodium hexametaphosphate to a water supply varies from $1.00 to $1.50 per million gallons for each part per million added. Thus, if two parts per million is added at a cost of about $2.50 per million gallons treated the annual cost would be about $900 per year for a water system supplying one million gallons per day or about $.09 per capita per year. This cost is not excessive if corrosion is inhibited, "red water" conditions are corrected and pipe tuberculation is reduced. The cost of sodium hexametaphosphate is from ten to fifteen cents per pound.

At present over 300 water supplies throughout the country are using metaphosphates. Results reported by a

few of these water supplies are noted below:

Fairhaven, Massachusetts

Some complaint was first reported after use of Calgon was begun due to initial disturbance of old iron oxide deposits, but after pH was lowered to 5.5. "red water" conditions disappeared and such conditions are now unknown. pH was lowered over a period of several months.

Winchester, Massachusetts

An original feed of 10 ppm of metaphosphate was used for one week, then dropped to 2 ppm. Results were satisfactory so a feed of 2 ppm was applied to the entire city system. Within one month all iron pickup in pipes had disappeared. The improvement of conditions was greatly accelerated by thorough flushing of mains to increase rate of flow and remove loose deposits of iron oxide.

Sumter, South Carolina

Sumter, South Carolina suffered periodically from "wild water". This was caused by the necessity of turning into the system a well with iron content of 3.8 ppm during periods of high demand. The water was "tamed" ~~in~~ the well water with high iron content. Results were so satisfactory that the well with high iron content was kept in constant use.

Canton, Ohio

Results were similar to Sumter, South Carolina in that a well with 1.5 ppm iron had to be turned into the distribution system during periods of high demand. Addition of 3 ppm of metaphosphate corrected all "red water" troubles.

Berwind, West Virginia

Berwind water supply is treated by the lime-soda method at the rate of 400,000 gallons daily. Considerable "after precipitation" of carbonate deposit developed, both on filter sand and in lines and valves of the filtration plant. 2 ppm of "Naloo No. 18 Ball" (a 68% phosphate, 15% sodium carbonate glass) eliminated all difficulties.

Nitro, West Virginia

The city of Dunbar, West Virginia is supplied with water by a seven mile long pipe line ffom Nitro. The line was cleaned mechanically, resulting in widespread "red water" complaints. Iron content of the water ran as high as 3.4 ppm.

Calgon was applied in a concentration of 10 ppm for two days, then reduced to 5 ppm for two days, then applied in a concentration of 1 ppm for six months. Application was at the Nitro end of the seven mile line.

No residual of metaphosphate was found in the Dunbar end of the line after six months time. Iron content rose

and fell during the period of application. Just as good results were obtained after use of metaphosphate was discontinued as during the time of use. Sodium hexametaphosphate did not demonstrate any capacity to inhibit corrosion or reduce "red water."

Sioux Falls Army Air Base, South Dakota

125 failures of hot water systems per year was reduced to zero failures per year by adding 5 ppm of sodium septaphosphate.

Las Vegas Army Air Base, New Mexico

Numerous complaints of "red water" were received each day. 2 ppm of Calgon reduced "red water" to almost zero. Four months flushing of mains, coupled with application of Calgon in the above concentration cleared mains, showed a great reduction in the rate of hot water tank corrosion and greatly improved the entire system with respect to head losses.

CONCLUSIONS

1. Metaphosphates hold iron and calcium in complex ion combinations if added before water is chlorinated or aerated. This action greatly reduces the effects of "red water", due to iron pickup in the pipe lines and to natural iron content of the water. Calcium carbonate scale is greatly reduced by the addition of metaphosphate to water distribution systems and calcium carbonate growth is prevented upon sand grains of sand filters by small concentrations of the chemical.

2. Metaphosphates in many cases have proved very helpful in the reduction and even total elimination of corrosion in pipe distribution systems. However the chemical has not been successful in all cases and the ability of metaphosphates to inhibit corrosion in all cases is in question. Many conflicting reports, both pro and con, are reported in the literature.

3. Metaphosphates are non toxic in concentrations employed for inhibiting corrosion and reducing scale and "red water".

4. Volume and velocity of water passing through pipe mains appear to be as important as quantity of phos-

phate used. Large pipes require lower concentrations for good results than small pipes.

5. Application of metaphosphates at the rate of 0.2 ppm to 10 ppm is recommended, depending upon results desired, pipe velocity, volume of flow and length of time over which the metaphosphate is used.

6. Use of metaphosphate is not unduly expensive if corrosion is inhibited or "red water" corrected.

7. Inhibiting of corrosion in hot water systems is more difficult than in cold water systems and a concentration of 25 ppm or more of metaphosphate is often required for satisfactory results. This is most easily provided by a slow dissolving phosphate glass such as Micromet.

8. Metaphosphates have no effect upon the softening and iron removing capacity of a zeolite softener. Their use previous to lime-soda softening will interfere with the softening unless a slight excess of alum, iron sulfate, or other coagulent is added to adsorb the metaphosphate.

TESTS TO STUDY THE CORROSION OF STEEL BARS UNDER VARIOUS CONDITIONS WHICH MIGHT EXIST IN MUNICIPAL AND OTHER WATER SUPPLY SYSTEMS

GENERAL DISCUSSION OF TESTS WITH STEEL BARS TO STUDY THE VALUE OF SODIUM HEXAMETAPHOSPHATE IN CONTROLLING CORROSION IN IRON AND STEEL PIPES OF WATER SYSTEMS

Shortly after the end of Warld War II Professor Edward F. Eldridge of Michigan State College Engineer Experiment Station began a series of experiments with Sodium Hexametaphosphate, more commonly known by the trade name of Calgon. His purpose was to study the value of this chemical in controlling corrosion of iron and steel pipes. Professor Eldridge served as an employee of the U. S. Army during the war and in his work used Calgon extensively in combating corrosion of pipes and plumbing fixtures in army camps. It is his opinion that several million dollars was saved during this period by using Calgon in corrosion control.

The author has studied the results of these experiments, and has used them as a basis for the studies described in this paper.. Some changes have seemed wise in view of results obtained from the early experiments.. For instance, Professor Eldridge originally began his experiments with the idea of using the iron content of the water from bottles (after tests) as an index of corrosion. Loss of weight of bars, however, proved a better and more easily studied index of corr -

osion, and during his later experiments he used this method of measuring corrosion of the bars. This latter method is that used in this series of tests.

In performing these experiments the author has rebuilt the apparatus used by Professor Eldridge, and has found it a satisfactory method for making a general study of the value of Sodium Hexametaphosphate under various conditions such as might exist in water systems.

DESCRIPTION OF APPARATUS AND PROCEDURE USED IN TESTS WITH STEEL BARS AND VARIOUS STRENGTHS OF CALGON SOLUTION

APPARATUS

1. Mechanism to revolve rods in quart milk bottles.
2. 12 one quart milk bottles.
3. 12 quarter inch cold-rolled steel bars 5½ inches long.
4. 12 rubber stoppers fitted with short pieces of glass tubing to act as bushings for stirring rods.
5. 12 six-inch lengths of stirring rods to connect stirring mechanism to steel rods.
6. Short pieces of rubber tubing to fasten steel rods being tested to glass stirring rods.

PRELIMINARY PROCEDURE

1. Clean steel rods thoroughly.

a. Wash and remove dirt and rust with steel wool.

b. Wash with carbon tetrachloride.

c. Wash with alcohol, dry, and place in desiccator. Do not touch with hands after alcohol wash.

d. When dry weigh to nearest 0.0001 gram.

NOTE: This procedure is used after each test run except that steel wool is used to clean bars before first test only, and is omitted thereafter. Bars are marked with file marks for identification.

MAKE UP WATER

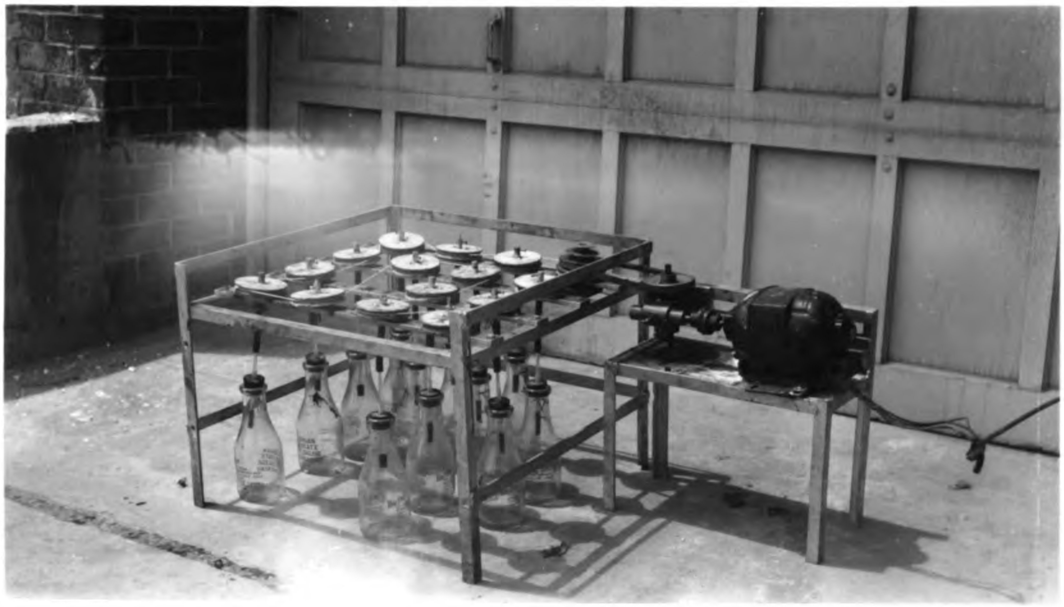
1. Draw off five gallons of tap water.
2. Make dissolved oxygen test on water.
3. Siphon the water to each bottle, filling completely. Add variables and make pH tests.
4. Attach weighed bars to glass stirring rods with short pieces of rubber tubing.
5. Insert stopper to fill the glass tube in the cork and remove all air bubbles.

NOTE: Each bottle is calibrated for volume of liquid it contains during actual test, that is with glass stirring rods, steel rods, and rubber tubing in position for operation. Calgon is made up in 1000 parts per million strength and added to test milk bottles by means of pippettes.

PROCEDURE

1. Allow test bars to rotate at specified speed (usually 42 rpm) for 24 or 48 hours.
2. Stop stirring apparatus. Remove test bars and wipe dry. Clean with hydrochloric acid solution, wash with distilled water, rinse with carbon tetrachloride and alcohol, place in desiccator and weigh.
3. Insert specially prepared stopper for withdrawing water after tests, shake bottle and withdraw samples for dissolved oxygen and pH tests.

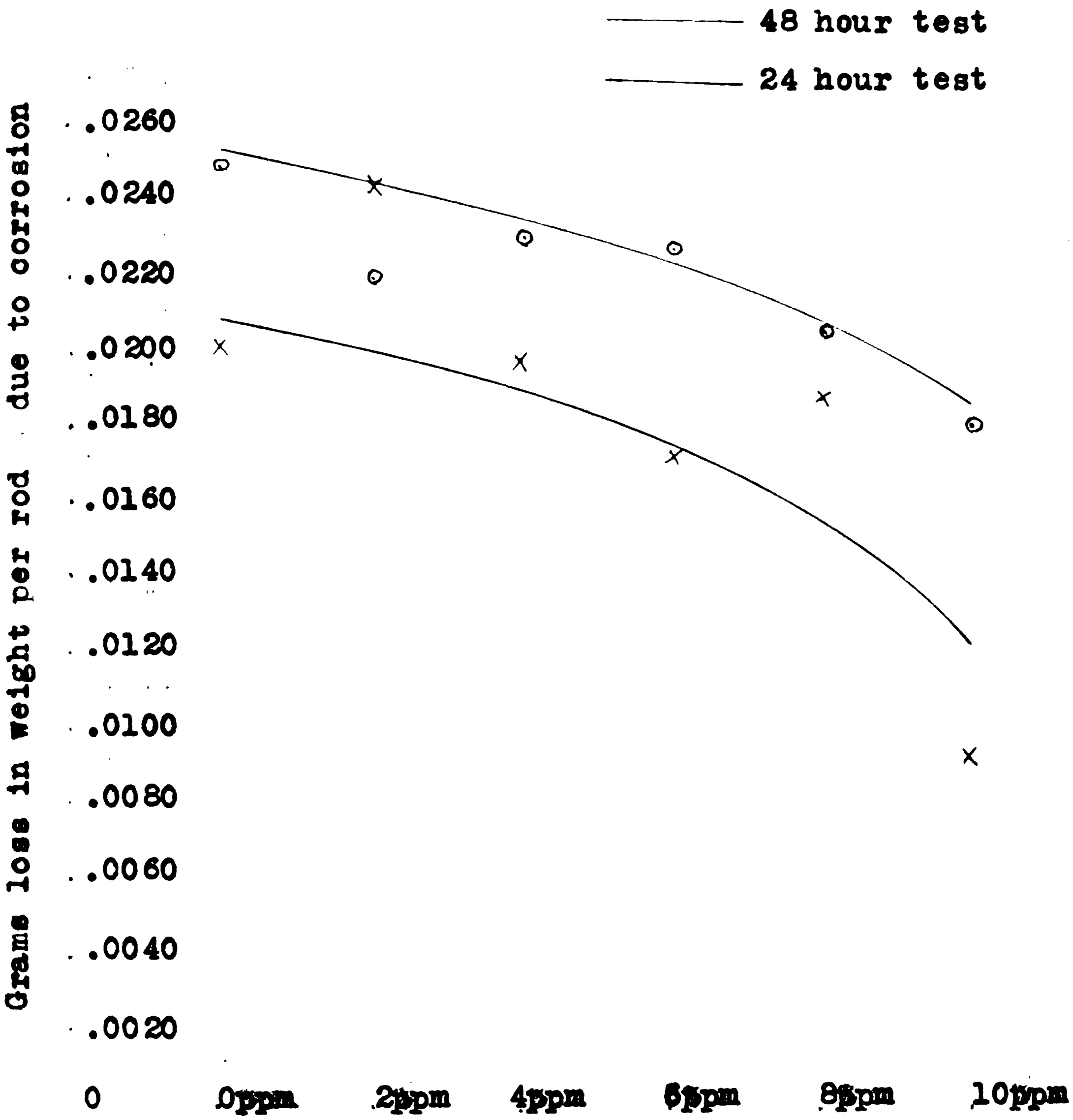
4. Make dissolved oxygen and pH tests.
5. Record results and plot applicable curves.



STIRRING APPARATUS USED IN TESTS WITH STEEL RODS

TEST NUMBER ONE

Curve indicating loss in weight of steel bars with various additions of Calgon (in ppm)



Parts Per Million Calgon added

TABULATION OF RESULTS FROM TEST # 1. MICHIGAN STATE COLLEGE TAP WATER WITH CALGON SOLUTION

Bottle	Capacity (ml)	Calgon added (ppm)	Wt of rod before test (grams)	Wt of rod after test (grams)	Loss in weight (grams)
1	928	0	35.1941	35.1737	.0203
2	920	2	35.2914	35.2670	.0244
3	924	4	35.0860	35.0662	.0198
4	916	6	35.2376	35.2205	.0173
5	920	8	35.2448	35.2269	.0189
6	919	10	35.3440	35.3353	.0093
7	923	0	34.8910	34.8661	.0249
8	921	2	35.3459	35.3238	.0221
9	928	4	35.2442	35.2211	.0231
10	932	6	35.0930	35.0702	.0228
11	919	8	35.1606	35.1400	.0206
12	917	10	34.8900	34.8719	.0181

Remarks:

Dissolved oxygen bottle 1 before test 8.6. After 24 hours 2.4. Dissolved oxygen bottle 7 before test 8.6. After 48 hours 1.7. Rods in bottles 1-6 exposed 24 hours, bottles 7-12 exposed 48 hours

Discussion of Test Number One

Test number one was intended as a trial test in measuring the value of Sodium Hexametaphosphate (Calgon) as a means of deterring the corrosion of iron and steel in water pipes. Procedure consisted of adding various amounts of Calgon to test bottles, filling with water, inserting weighed steel rods, making a dissolved oxygen test of the water used, and revolving the rods for periods of 24 and 48 hours. Following these periods of exposure the rods were washed together in dilute solutions of hydrochloric acid, carefully weighed, and loss of weight determined. Loss in weight was used as an index of corrosion, and loss of weight has been plotted against parts per million of Calgon used on the accompanying sheet.

Of particular interest is the tendency of loss of weight to decrease with increased amounts of Calgon. The sharpest break in the curve is noted to be between 8 and 10 parts per million strength. It must be noted however that small increases in the amounts of Calgon used does not always result in similar decreases in loss of weight. On the contrary increased amounts of Calgon seem to cause noticeable changes in weight losses at certain points in the curve only.

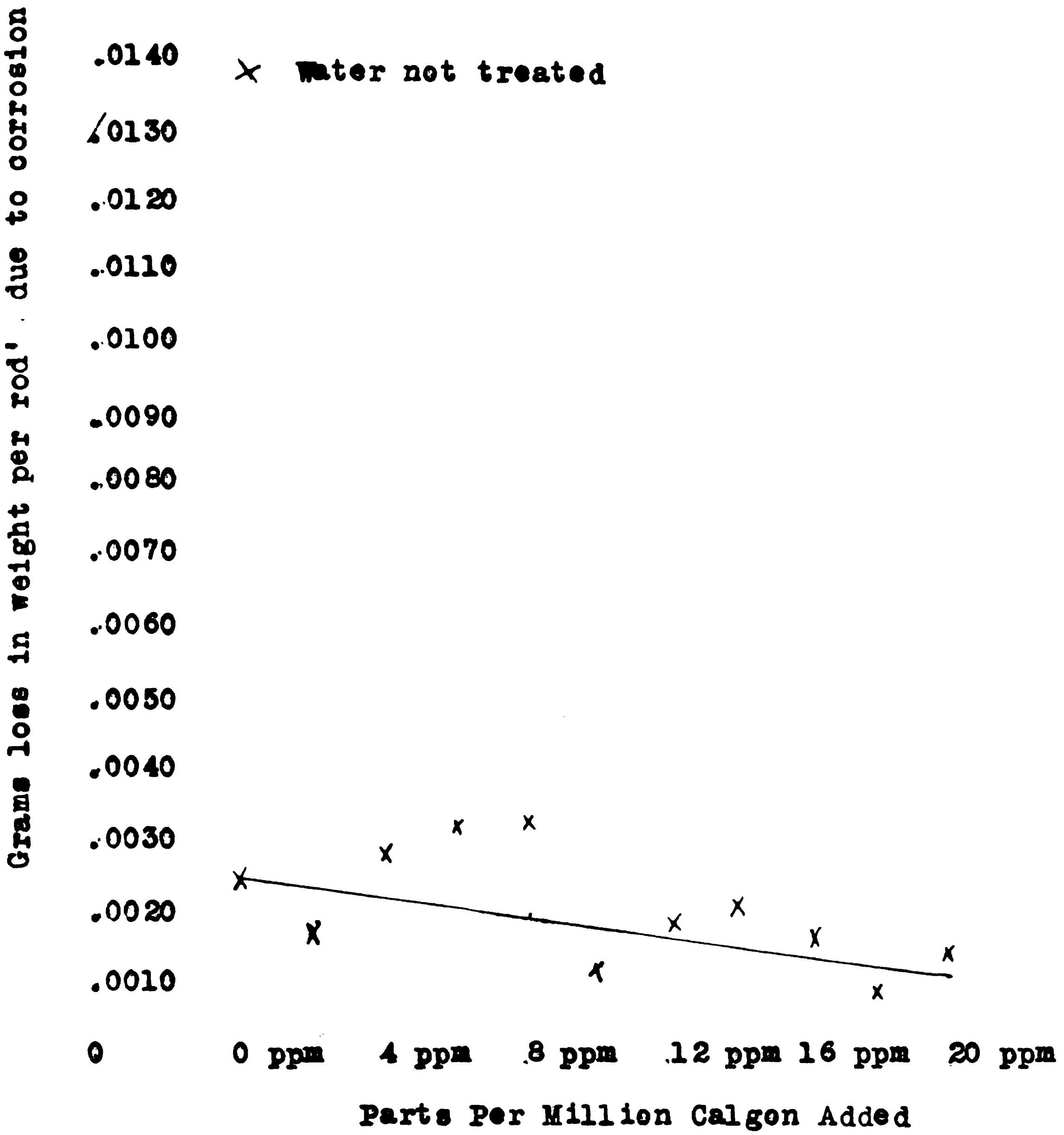
Also of interest is the flatness of the 48 hour curve as compared to the 24 hour curve. This is obviously caused by the almost complete chemical combination of most of the dissolved oxygen with iron during the first 24 hours of exposure. The rate of corrosion is sharply reduced during the second 24 hour period, particularly with respect to the rods exposed to water containing little or no Calgon. Dissolved oxygen at the beginning of the test was 8.5 ppm, after 24 hours 2.4 ppm and after 48 hours 1.6 ppm, thus indicating that the greater part of the combination of iron with oxygen to form oxides and hydroxides took place during the first 24 hours. The curve showing loss of weight with various strength Calgon solutions definitely shows that oxygen dissolved in water is the most important agent of corrosion, and that the rate of corrosion was several times higher during the first 24 hours when an ample supply of oxygen was present than during the second 24 hour period when oxygen was largely absent.

Since the rods were all washed together in dilute solutions of hydrochloric acid, loss of weight of the rods seems to be an excellent method of measuring corrosion. After washing with hydrochloric acid solution all rods were a bright gray color, indicating that all ferric oxide and hydroxide were removed. An even stronger argument for believing that this procedure is a true measure of corrosion of the steel bars is the appearance of the test bottles after the 24 hour test. Number one bottle was very red in color (a typical "red water") and contained a very heavy concentration of red precipitate. No Calgon was added to bottle number one. Number six bottle, containing 10 parts per million Calgon was still reasonably clear after a 24 hour period, slightly red, and with a very light precipitate. The other four 24-hour test bottles varied in color between these extremes, very much in line with the losses of weight noted. No such comparison could be made after 48 hours of exposure because all bars had become quite corroded after that time.

Dissolved oxygen tests were made on bottles containing untreated water (no Calgon) only. No pH measurements were attempted on this first test. Tests in which particular attention has been paid to these factors, together with tests with heavier concentrations of Calgon are shown later.

TEST NUMBER TWO

Curve indicating loss in weight of steel bars with various additions of Calgon (in ppm) added to Michigan State College tap water from which dissolved oxygen has been removed



TABULATION OF RESULTS FROM TEST # 2. MICHIGAN STATE COLLEGE TAP WATER WITH ZERO DISSOLVED OXYGEN VARIOUS STRENGTH CALGON SOLUTIONS ADDED TO WATER

Bottle	Dissolved oxygen (ppm)	Calgon added (ppm)	Wt of rod before (grams)	Wt of rod after (grams)	Loss in weight (grams)
1.	8.2	0	35.1737	35.1599	.0138
2.	8.2	20	35.2700	35.2685	.0015
3.	0	2	35.0662	35.0645	.0017
4.	0	4	35.2205	35.2176	.0029
5.	0	6	35.2269	35.2234	.0033
6.	0	8	35.3357	35.3324	.0033
7.	0	10	34.8661	34.8648	.0013
8.	0	12	35.3238	35.3219	.0019
9.	0	14	35.2211	35.2189	.0022
10.	0	16	35.0702	35.0685	.0017
11.	0	18	35.1400	35.1391	.0009
12.	0	20	34.8719	34.8704	.0015

Remarks:

Rods were exposed to solutions for 24 hours. They were stirred for 12 hours, then left in solution without stirring for 12 hours.

Discussion of Test Number Two

Test number two was performed to observe the relationship of dissolved oxygen to the corrosion of steel bars, and to find out whether Calgon is an effective means of combatting corrosion in waters containing very low quantities of dissolved oxygen.

Test bottle number one was used as a control, that is no Calgon was added, and the dissolved oxygen content was permitted to remain the same as Michigan State College tap water. Test bottle number two also contained a normal amount of dissolved oxygen, (8.2 ppm) but 20 parts per million of Calgon was added to this bottle. All dissolved oxygen was removed from the other ten test bottles, and various amounts of Calgon were added, varying from 2 parts per million for test bottle three to 20 parts per million for test bottle twelve.

Results from this test are interesting. Test bottle one, the control, lost .0138 grams of weight due to corrosion. The bottle contained a typical "Red Water" after 24 hours of testing, with a light sediment of red percipitate in the bottom. The rod was covered with a light film of rust, which stained a cloth used for wiping the rods. This loss of weight of .0138 grams

compares with .0203 grams of weight lost by the rod exposed to similar conditions in test one. This variance in loss of weight is probably explained by the slight variation in procedure, that is the rods were rotated a full 24 hour period during test one, while test two consisted of a 12 hour period of stirring followed by 12 hours of exposure to the solutions without stirring. This would seem to indicate that corrosion proceeds at a higher rate when water is in motion than when it is still, though of course this single test can be used as an indication only.

All rods in solutions from which dissolved oxygen had been removed were still of a bright gray color after 24 hours of exposure, indicating a very slight corrosion. A comparison between test bottles one (which contained 8.2 ppm of dissolved oxygen and suffered a weight loss of .0138 grams) and three (which contained no dissolved oxygen and suffered a weight loss of only .0015 grams) shows clearly that iron and steel corrosion in water pipes is caused by the dissolved oxygen content of the water. It is true that bottle three contained 2 parts per million of Calgon, but this amount has only a slight influence on the rate of corrosion.

A comparison of weight losses in bottles containing various strengths of Calgon shows that it has helped only slightly in reducing corrosion in these oxygen-free waters.

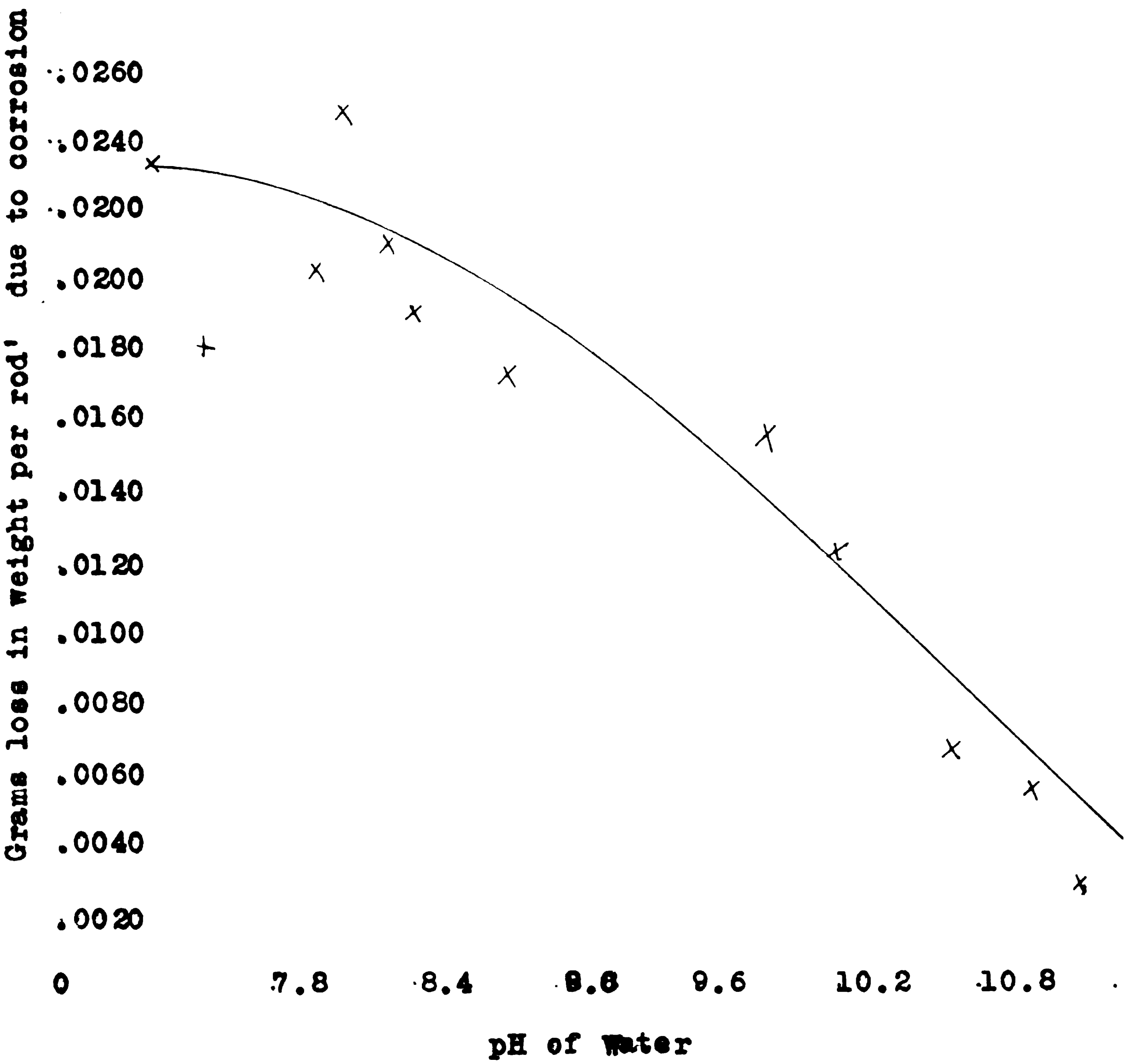
All bottles from which dissolved oxygen had been removed contained almost completely unstained waters after the test. A comparison between the colors of the waters after the test is in many ways as good an indication of corrosion as the loss in weight, and as indicated above, in this case showed a typical red water in the bottle containing 8.2 parts per million of dissolved oxygen and no Calgon, and almost no change in color in bottles containing no dissolved oxygen.

Dissolved oxygen was removed from bottles three through twelve by adding 150 parts per million of sodium sulphite to each bottle. This chemical combines with dissolved oxygen to form sodium sulphate, and is sometimes used for removing small quantities of dissolved oxygen from a water of a municipal water system. It must be used with great care, however, since it is poisonous, and can be used in only very small quantities. As the figure of 150 parts per million indicates, a considerable quantity of this chemical is necessary to remove all of the dissolved oxygen from a water.

Bottle two, containing 8.2 parts per million of dissolved oxygen and 20 parts per million of Calgon demonstrates that this strength solution of Sodium Hexametaphosphate is very effective in reducing corrosive affect of the dissolved oxygen in Michigan State College tap water. The rod removed from this bottle after 24 hours of exposure was almost as bright and shiney as when put in, and only .0015 grams of weight loss was noted. Almost no staining of the water containing 20 parts per million Calgon was noted.

TEST NUMBER THREE

Curve indicating loss in weight of steel bars exposed for 24 hours to Michigan State College tap water which was adjusted for various pHs by the addition of sodium hydroxide and calcium hydroxide



TABULATION OF RESULTS FROM TEST #3. MICHIGAN STATE COLLEGE TAP WATER WITH VARYING pH

Bottle	pH before test (ppm)	pH after test (ppm)	Wt of rod before (grams)	Wt of rod after (grams)	Loss in weight (grams)
1	7.4	7.2	35.1536	35.1303	.0233
2	7.5	7.5	35.2630	35.2449	.0181
3	7.9	8.0	35.0577	35.0375	.0202
4	8.2	8.0	35.2176	35.1929	.0247
5	8.5	8.1	35.2234	35.2024	.0210
6	8.7	8.0	35.3324	35.3134	.0190
7	9.2	8.5	34.8648	34.8475	.0173
8	10.0	9.8	35.3219	35.3064	.0155
9	10.3	10.2	35.2189	35.2067	.0122
10	10.8	10.6	35.0685	35.0618	.0067
11	11.1	10.8	35.1391	35.1335	.0056
12	11.4	11.1	34.8704	34.8676	.0028

Remarks:

7.4 represents tap pH of Michigan State College water.

pH of bottles 2-6 raised by addition of lime $Ca(OH)$.

pH of bottles 6-12 raised by addition of sodium hydroxide solution $Na(OH)$. No chemical added to bottle #1.

Discussion of Test Number Three

Test number three is a study of the effect of pH on rate of corrosion of steel bars. Performance of this test consisted of making up a saturated solution of lime water and decanting the clear solution. This clear lime water was added to bottles two to six inclusive in increments of five milileters - that is, five milileters to bottle two, ten milileters to bottle three, fifteen milileters to bottle three etc. Bottle one was left untreated, and used as a control for comparison purposes. Because of the reaction of lime with the bicarbonate hardness of the water, a percipitate was noted after thirty milileters had been added to bottle seven. For this reason, bottles seven through twelve were treated with sodium hydroxide solution to raise the pH. Explaination of the formation of the percipitate lies in the combination of lime water with dissolved carbon dioxide in the water until all carbon dioxide was removed. Following this removal of carbon dioxide the lime water was free to react with the bicarbonate hardness of the water. pH of the water was raised by the combination of lime water with carbon dioxide to form Calcium Bicarbonate, but as soon as this reaction was completed further additions of lime water caused a fall in pH due to removal of the bicarbonate alkalinity when lime combined with calcium bicarbonate to form non-soluble calcium carbonate.

Rods were inserted in bottles as usual, and revolved for periods of twenty four hours in the test solutions, following which they were removed, inspected, cleaned with hydrochloric acid and weighed.

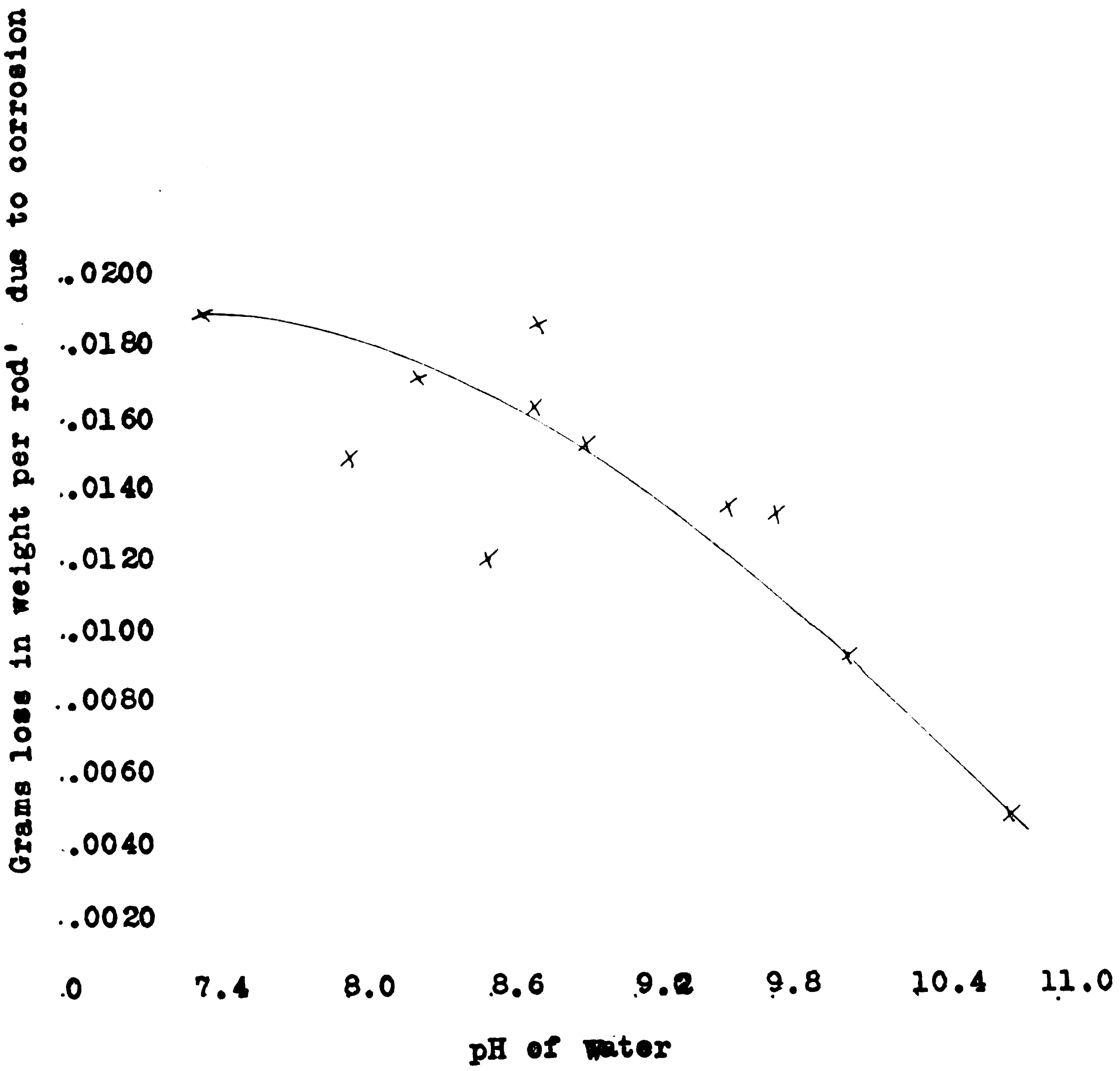
Rods one through six showed a strong tendency to corrode. It should be noted that none of the solutions in these six bottles showed a pH higher than 8.1 after twenty four hours of exposure. This pH is slightly above that of Michigan State College tap water, but not enough so to have much effect on the rate of corrosion. It is noted that the rate of corrosion for these waters with pH up to 8.1 was only slightly less than in bottle one, which was not treated at all. Beginning with rod seven, which was exposed to water of pH 8.5 to 9.2, a definite decrease in the rate of corrosion was noted. When pH reached the value of 10.6 to 10.8 (for rod ten) a very sharp decrease in the rate of corrosion was noted. Indeed it can be seen that a pH above 10.0 is very effective in reducing corrosion, while values below this have only a tendency to reduce the rate of corrosion.

As in previous tests, inspection of test bottles and of rods after testing showed results much in line with results obtained by studying loss of weight of the steel rods. Bottles one through six contained typical red water after 24 hours of exposure, although the color was lighter in bottles with higher pHs. Rods one through six showed considerable corrosion. Bottles nine through twelve, all with pH higher than 10.2 showed no discoloration of the water, but rods were slightly corroded. Bottles eleven and twelve with pH higher than 10.8 were still very clear, and these rods were still of a bright gray color after twenty four hours of testing.

It should be observed that this short test does not truly measure the value of high pHs as a means of combating corrosion, since one of the principal values of high pHs are their tendency to cause a protective coating of calcium carbonate to be laid down. This is of course a long time process, and no such coating could be laid down during this short test, and under the methods of testing employed.

TEST NUMBER FOUR

Curve indicating loss of weight of steel bars exposed for 24 hours to Michigan State College tap water treated to 23 parts per million hardness with zeolite sand, and adjusted to various pHs by the addition of sodium hydroxide



TABULATION OF RESULT FROM TEST #4. MICHIGAN STATE COLLEGE TAP WATER, TREATED TO 26 PARTS PER MILLION HARDNESS WITH SODIUM ZEOLITE, AND WITH VARYING pHS

Bottle	Mean pH	Dissolved Oxygen removed (ppm)	Rod's loss in weight (grams)
1	7.4	5.6	.0189
2	8.0	7.6	.0150
3	8.3	4.8	.0176
4	8.6	4.8	.0122
5	8.8	5.2	.0188
6	8.8	5.2	.0165
7	9.0	4.2	.0154
8	9.5	3.6	.0136
9	9.8	5.0	.0135
10	10.1	2.4	.0095
11	10.8	0	.0053
12	10.8	0	.0053

Remarks:

7.4 represents tap pH of Michigan State College water.

pH of bottles 2 through 12 raised by adding sodium hydroxide solution Na(OH)

Discussion of Test Number Four

Test number four was performed to observe the relation of pH to the rate of corrosion of steel bars exposed to zeolite softened waters.

This test was performed in much the same manner as test three, that is, waters of various pHs were made up by adding sodium hydroxide solution to water softened to twenty five parts per million hardness with zeolite sand. Bottle one was treated for hardness only, that is no sodium hydroxide was added, and this bottle was used as a control. Note: Michigan State College water normally has a hardness of about three hundred fifty parts per million.

A careful note of dissolved oxygen in each bottle before and after the usual 24 hours test was made, and these values are shown in tabulating the results for this test.

Although a general relationship between oxygen removed and loss in weight of the bars can be noted, no definite relationship between these two quantities can be determined. It is of interest that no change in the amount of dissolved oxygen in bottles eleven and twelve was observed during the period of testing, and loss of weight for rods exposed to waters in these two bottles is small when compared to that of other rods used in the test.

Curves obtained from this test compare very much with those obtained from a similar test with Michigan State College tap water from which no hardness had been removed.

No considerable change in loss of weight is to be seen until pH becomes 10 or higher. At this point a very radical change in the rate of corrosion is observed. Waters with pH of 10 or higher were unstained after 24 hours of testing, while waters of pH below this value were stained to varying degrees, with waters below pH 9.6 showing a typical "red water" color.

All waters treated with sodium hydroxide were observed to have covered the rods with a slimy coating, which no doubt provided considerable protection against the corrosive effect of the dissolved oxygen in the water. Rods nine and eleven, pH 9.8 and 10.1 were noted to have been badly corroded in a few spots only, these particular points no doubt being points where a slight variatian of purity of the metal occured.

TABULATION OF RESULTS FROM TEST #5. MICHIGAN STATE COLLEGE TAP WATER, TREATED TO 23 PARTS PER MILLION HARDNESS WITH SODIUM ZEOLITE, AND WITH VARIOUS AMOUNTS OF CALGON SOLUTION ADDED

Bottle	Calgon added (ppm)	Rod's loss in weight (grams)
1	0	.0169
2	2	.0155
3	4	.0155
4	6	.0167
5	8	.0154
6	10	.0088
7	12	.0131
8	14	.0056
9	16	.0168
10	18	.0138
11	20	.0155
12	22	.0156

Remarks:

Steel rods used were the same as those used in previous four tests, ¼ inch in diameter, and 5 inches long. Weight of all bars is about 35 grams. Calgon solution used was two weeks old.

Discussion of Test Number Five

Test number five was performed to observe the effect of various additions of Calgon to zeolite softened water on the rate of corrosion of steel bars.

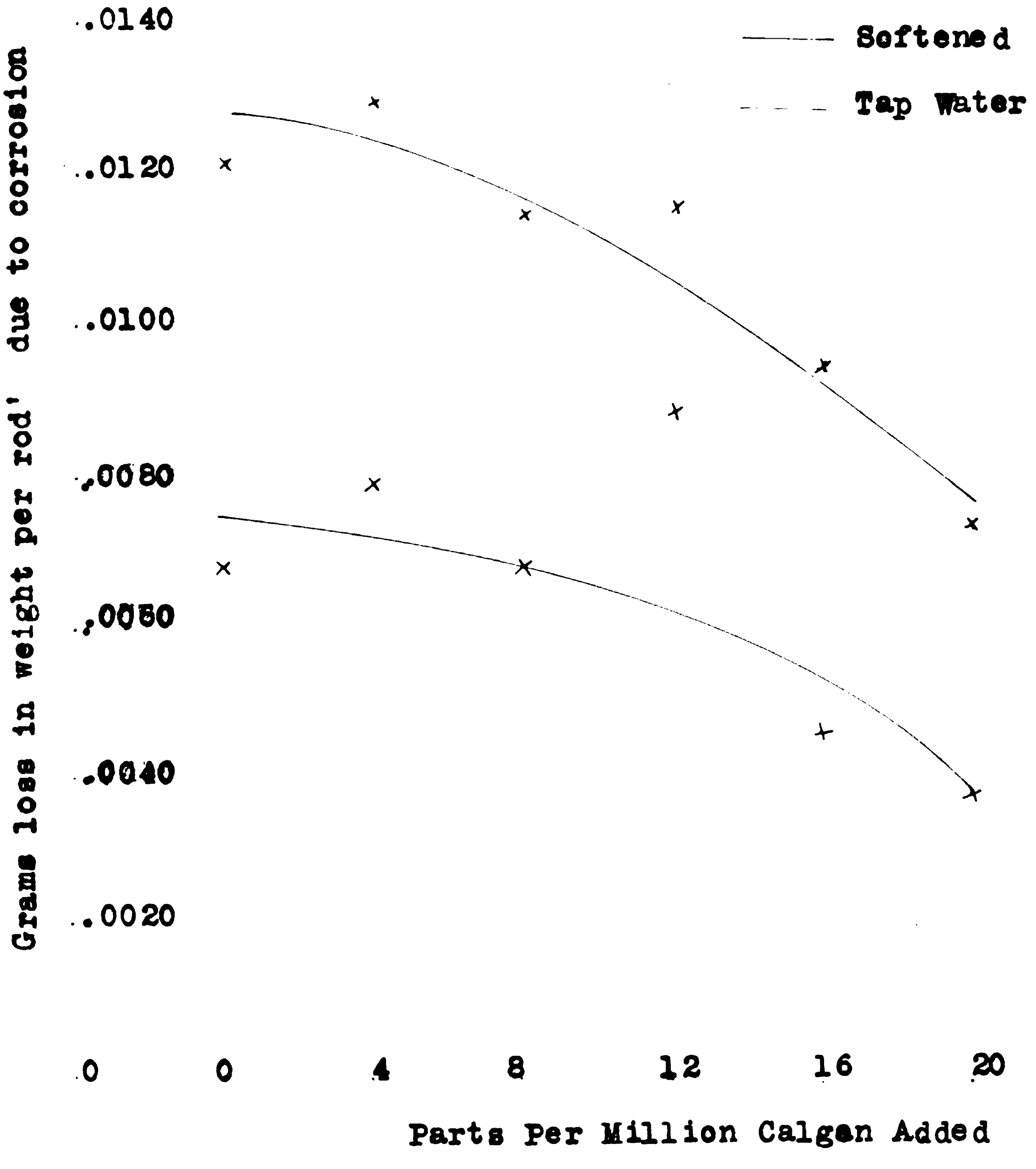
Results of the test would seem to indicate that Calgon does not inhibit corrosion of the bars in the zeolite softened water used. No appreciable difference between losses of weight with and without additions of Calgon is to be noted.

Other investigators, particularly G. B. Hatch and Owen rice, both of Hall Labratories, Pittsburgh, Pennsylvania, have observed that glassy phosphates seem to have little value when used in zeolite softened waters unless some calcium is present. Zeolite softening changes calcium salts to sodium salts. Experiments seem to indicate that calcium must be present with metaphosphates in a ratio of at least 0.2 parts calcium to 1.0 part of metaphosphate in order to obtain satisfactory results when glassy phosphates are used to inhibit corrosion.

A further test, test ten, will repeat test five using a water of very high oxygen content to note if results similar to those from this test are obtained.

TEST NUMBER SIX

Curves indicating loss of weight of steel bars exposed to Michigan State College Tap water and to Michigan State College water softened to 40 parts per million hardness with a zeolite water softener. Various amounts of Calgon added to each water. All rods polished with steel wool before test.



TABULATION OF RESULTS FROM TEST # 6. MICHIGAN STATE COLLEGE TAP WATER COMPARED FOR CORROSIVENESS WITH MICHIGAN STATE WATER SOFTENED TO 40 PARTS PER MILLION HARDNESS WITH A ZEOLITE SOFTENER. DISSOLVED OXYGEN VARIED, RODS POLISHED BEFORE TEST

Bottle	Calgon added (ppm)	Rod's loss in weight (grams)	Remarks
1	0	.0122	Softened
2	4	.0092	Softened
3	8	.0115	Softened
4	12	.0116	Softened
5	16	.0095	Softened
6	20	.0074	Softened
7	0	.0074	Tap
8	4	.0079	Tap
9	8	.0074	Tap
10	12	.0089	Tap
11	16	.0026	Tap
12	20	.0018	Tap

Remarks:

Dissolved oxygen of tap water 3.2, of softened water 6.0

Discussion Of Test Number Six

Because of poor results obtained with the use of sodium hexametaphosphate in reducing the corrosiveness of zeolite treated water in the previous test (number five) the test was rerun with certain alterations which permitted results with zeolite water to be compared with those obtained with tap water.

Rods were first polished with steel wool in order to remove any incrustation or other protective film which remained from previous tests, and then weighed to four places as usual. Six bottles were then filled with tap water with a dissolved oxygen content of 3.2 parts per million and six were filled with zeolite softened water (40 parts per million hardness remaining) with a dissolved oxygen content of 6.0 Addition of Calgon solution were then made to give concentrations of 4 to 20 parts per million for both softened and tap water.

Because of the differences of dissolved oxygen content a comparison cannot be made between corrosion of bars in softened and in tap water. Rather, the test indicates that Calgon is effective in inhibiting corrosion of polished steel bars in both zeolite softened water and in

tap water.

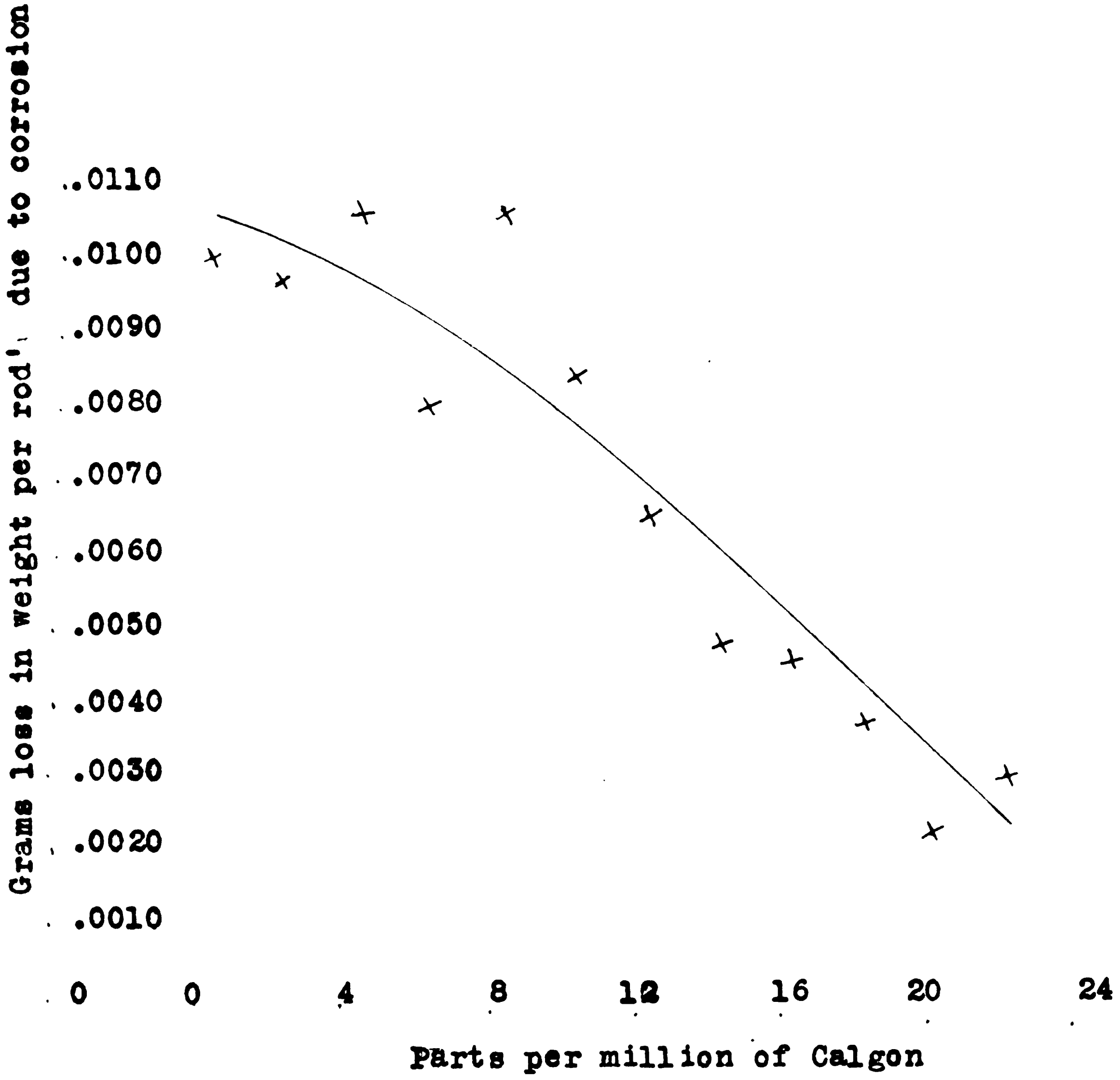
Polishing the bars removed a rather heavy outside film or skin which in the previous test (number five) was no doubt quite effective in inhibiting corrosion of all bars and no doubt, in part at least, explains the unsatisfactory results obtained in that test.

Results from test six, while showing that polished steel bars are protected to a considerable extent by glassy phosphate, does raise the question as to whether the chemical is so successful in inhibiting corrosion of unpolished steel bars. This question is studied in test number nine.

As usual, bottles containing stronger concentrations of glassy phosphate showed no "red water" while bottles with weak concentrations of phosphate or no phosphate at all were badly stained with iron rust.

TEST NUMBER SEVEN

Curve indicating loss of weight of steel bars exposed for 24 hours to Michigan State College tap water with a dissolved oxygen content of about 6.2 and with various amounts of calgon solution added



TABULATION OF RESULTS FROM TEST #7. MICHIGAN STATE COLLEGE WATER WITH VARIOUS ADDITIONS OF CALGON SOLUTION AND LOW OXYGEN CONTENT

Bottle	Calgon added (ppm)	Rod's loss in weight (grams)
1	0	.0101
2	2	.0098
3	4	.0108
4	6	.0081
5	8	.0108
6	10	.0086
7	12	.0067
8	14	.0050
9	16	.0048
10	18	.0040
11	20	.0026
12	22	.0034

Remarks:

All bottles contained waters with dissolved oxygen content of about 6.2 at beginning of test. This compares with dissolved oxygen contents of 7.6 to 8.2 for other tests with calgon.

Discussion of Test Number Seven

Test number seven varied from previous tests with Calgon and Michigan State College tap water in that larger amounts of Calgon were applied to the water than previously, the test was begun with a lower dissolved oxygen content (6.2 as compared with about 8.0) and the stirring apparatus was run for 16 hours, then stopped for 8 hours during the 24 hour test. In other respects the standard prodedure outlined in previous tests was followed.

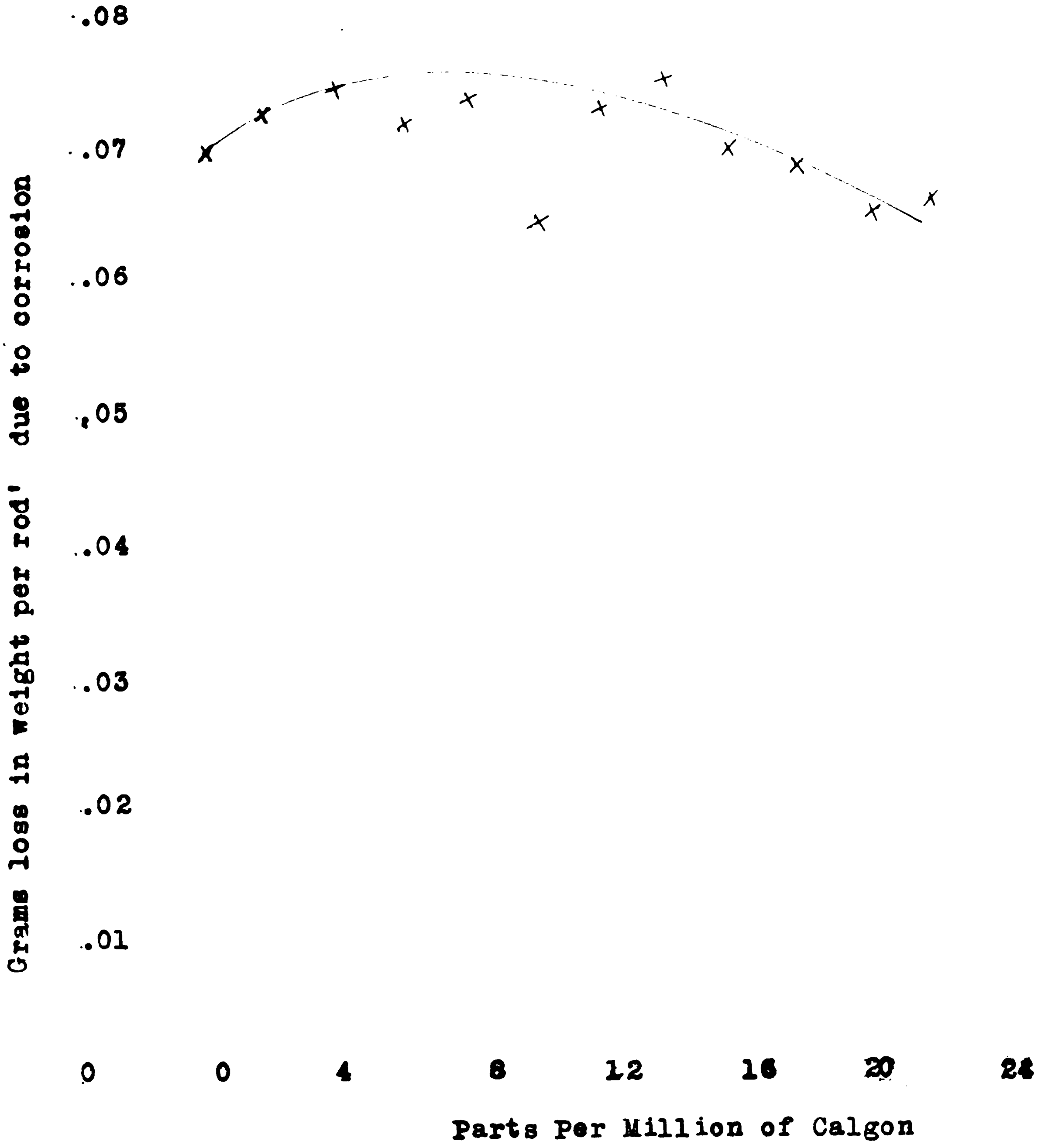
A plotting of loss of weight against amount of Calgon used shows a very considerable reduction in rate of corrosion with increasing amounts of Calgon. A comparison of bottles one through twelve after the test showed a typical "red water" in bottles one and two, with an increasing clearness and decreasing amount of red color as the amount of Calgon added increased. Bottles eleven and twelve, with 20 and 22 parts per million Calgon respectively, were almost completely clear after 24 hours of testing.

No doubt the erratic but steady decrease in rate of corrosion is explained in the varying purity of the metal of the bars, which in some cases overcomes the protective effect of the Calgon. Bars with slight impurities corrode much rapidly than the pure metal.

This test indicates that increased additions of Calgon doubtless leads to greater corrosion control, but amounts above 22 parts per million are not practical for water systems, and therefore are not of great interest to this particular study.

TEST NUMBER EIGHT

Curve indicating loss of weight of steel bars exposed for six days to Michigan State College tap water changed daily, and with various amounts of calgon solution added. Dissolved oxygen content average of about 7.0



TABULATION OF RESULTS FROM TEST # 8. MICHIGAN STATE COLLEGE TAP WATER WITH VARIOUS ADDITIONS OF CALGON SOLUTION, 7 DAY TEST WITH WATER CHANGED EVERY 24 HOURS, NEW CALGON SOLUTION ADDED

Bottle	Calgon added (ppm)	Rod's loss in weight (grams)
1	0	.0696
2	2	.0724
3	4	.0741
4	6	.0718
5	8	.0733
6	10	.0642
7	12	.0724
8	14	.0748
9	16	.0694
10	18	.0680
11	20	.0648
12	22	.0657

Remarks:

Tap water in bottles was changed every 24 hours, Calgon added each time water was changed. Dissolved oxygen content of water added varied from 6.8 to 7.2.

Discussion of Test Number Eight

Tests one through seven have consisted of adding Calgon solution or other chemicals to water, then inserting weighed steel rods and stirring rods for 24 or 48 hour periods in these solutions in such a manner as to exclude oxygen other than that dissolved in the water at the beginning of the test. These tests, while having great value in the study of corrosion under the various conditions involved do not approximate the exposure of water pipes to the corrosive effect of water. Water pipes are almost always exposed to a continuous supply of fresh water which usually caries a high amount of dissolved oxygen.

Test number eight was performed to observe the results which might occur in steel pipe which is used in large water lines. The steel rods were weighed as usual, then placed in the bottles containing various amounts of Calgon solution. At the end of 24 hours,the water was changed, and new additions of Calgon solution were made in the same strength as previously. After a second 24 hour period the water was changed as before, new additions of Calgon solution were made, and the rods were stirred in the stirring device for three 24 hour periods, with the water being changed every 24 hours, fresh amounts of Calgon being added each time. Finally the water was changed, Calgon solution added, and the rods allowed to sit for 24 hours in the bottles without stirring, Rods were then weighed as usual and loss of weight of rods computed. The entire test took about one weeks time. Dissolved oxygen of the tap water used was about 7.0

Results of the test indicate than an exposure of this type causes a continued corrosion of the bars during the entire time of exposure. A loss in weight of .07 grams average, as compared with a loss of weight of .02 grams or less in 24 hours shows that as long as a fresh supply of dissolved oxygen is present, corrosion will continue, although at a slower rate than during the first 24 hour period.

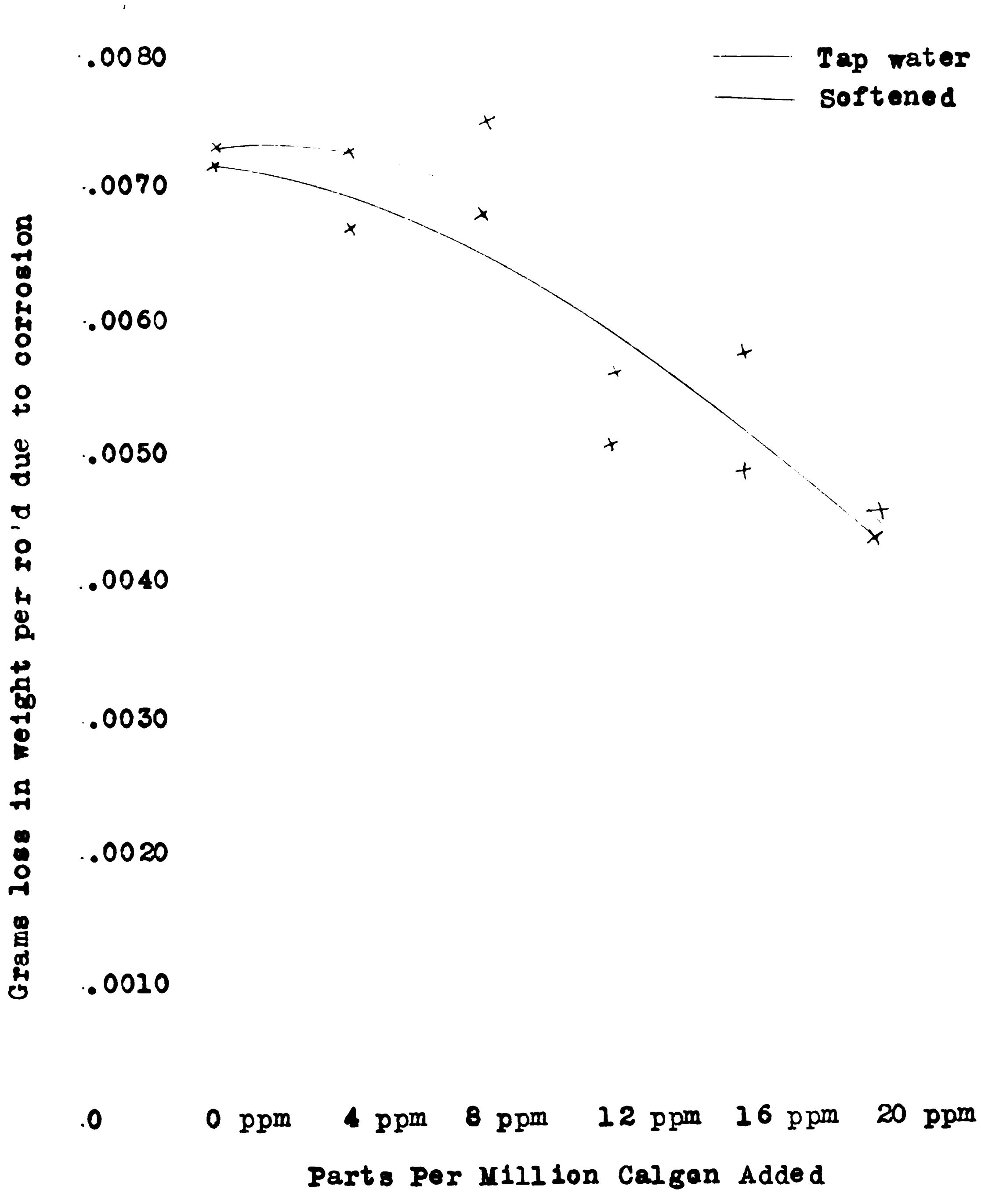
Observation of the bars demonstrated that corrosion occurs very slowly in quiet water, but very rapidly when the water is in motion. The bars were exposed to the water in the bottles for the first 48 hours without stirring, and during this period almost no rusting of the bars was observed. However, as soon as the stirring was begun a very rapid rusting of all the bars was noted. This was because motion of the bars removed the protective coating of hydrogen gas which had formed on the metal, permitting corrosion to progress at a very rapid rate.

Very slignt protection was provided the bars by the sodium hexametaphosphate in this test. Bars in solutions with 20 and 22 parts per million of Calgon showed a slightly lower loss of weight than any others,, but the difference is slight. This may be because the seven day period was not a long enough time to permit a heavy film of protective phosphate to form on the metal. The test shows that a wide variation in results is often obtained with phosphates, and that differences in these results are hard to explain. In this case no adequate explaination of the failure of the phosphate to provide protection can be offered, since previous tests have indicated that glassy phosphate usually gives considerable protection.

Observation of color of the water in bottles consistently showed that bottles having 6 parts per million or more of Calgon were clear, and contained no "red water" while water with less Calgon were badly stained. Thus, though there may be some question as to the ability of Calgon to provide protection in all cases, there is little question that the chemical has great value in combating "red water" by holding up iron ion, and preventing oxidation of ferrous oxide to the hydroxide, which is the objectionable red color of rusty water.

TEST NUMBER NINE

Curves indicating loss of weight of steel bars exposed to Michigan State College Tap water and to Michigan State College water softened to 40 parts per million hardness with a zeolite water softener. Various amounts of Calgon added to each water



TABULATION OF RESULTS FROM TEST # 9. MICHIGAN STATE COLLEGE TAP WATER COMPARED FOR CORROSIVE EFFECT WITH MICHIGAN STATE COLLEGE WATER SOFTENED TO 40 PARTS PER MILLION HARDNESS WITH A ZEOLITE WATER SOFTENER. SAME AMOUNTS OF CALGON SOLUTION ADDED TO BOTH WATERS

Bottle	Calgon added (ppm)	Rod's loss in weight (grams)	Remarks
1	0	.0072	Tap
2	4	.0067	Tap
3	8	.0068	Tap
4	12	.0051	Tap
5	16	.0058	Tap
6	20	.0044	Tap
7	0	.0073	Softened
8	4	.0073	Softened
9	8	.0075	Softened
10	12	.0056	Softened
11	16	.0049	Softened
12	20	.0046	Softened

Remarks:

Dissolved oxygen at start of test was 3.6 in tap water and 3.0 in softened water. Test was run for 24 hours

Discussion of Test Number Nine

In test number six a comparison was made of loss of weight of polished steel bars exposed to tap water and to zeolite softened water. In that particular test rods were polished with steel wool to remove film which might provide protection during time of exposure. Because of the good results obtained with glassy phosphates in that test it was felt that a similar test with unpolished bars would be of interest.

In test number nine bars which had been exposed for a period of one weeks time in test eight were washed with dilute hydrochloric acid as usual and weighed. Inspection of the bars indicated that a film of rather dark color remained on the bars after the acid wash.

Test was run as usual with tap water and with zeolite water softened to 40 parts per million hardness. Calgon was added in concentrations of 4 to 20 parts per million to both tap and softened water. Dissolved oxygen was 3.6 at the beginning of the test for tap water, as compared with 3.0 for the softened water.

A study of loss of weight of the bars shows that a slightly higher loss of weight was experienced by the bars exposed to zeolite softened water than to those exposed to tap water, even though the dissolved oxygen content of the tap water was slightly higher than that of the softened water. In addition, bars exposed to softened water were those removed from bottles with high concentrations of glassy phosphate in the previous test, giving these bars whatever protection might remain in the way of a phosphate-iron film or skin developed in the seven day exposure of test number eight.

A considerable reduction in rate of corrosion was noted in bars exposed to waters carrying higher concentrations of Calgon, both in the case of tap and softened water. The shape of "loss of weight curves" is generally the same for both waters.

This test would seem to indicate that softened waters are slightly more corrosive than unsoftened waters, and that glassy phosphate is helpful in inhibiting corrosion in both type waters. Results, as usual, were very erratic. Curves shown with this test indicate a <u>trend</u> only toward a lower rate of corrosion when larger additions of Calgon are made. Several points on the curves vary considerably from this general trend, and no explaination can be offered for these variations.

TABULATION OF RESULTS FROM TEST # 10. MICHIGAN STATE COLLEGE TAP WATER SOFTENED TO ZERO HARDNESS WITH SODIUM ZEOLITE, AND WITH VARIOUS AMOUNTS OF CALGON SOLUTION ADDED.

Bottle	Calgon Added (ppm)	Loss in Weight (grams)
1	0	.0227
2	2	.0230
3	4	.0230
4	6	.0247
5	8	.0248
6	10	.0217
7	12	.0260
8	14	.0230
9	16	.0243
10	18	.0249
11	20	.0242
12	22	.0201

Remarks:

Water softened to zero hardness, and aerated to dissolved oxygen content of 9.6.

Discussion of Test Number Ten

Test ten is a repeat of test five in which the effect of various additions of Calgon to zeolite softened water was studied with respect to the rate of corrosion of steel bars. Test ten is altered slightly however, in that a water of zero hardens was used instead of one of 23 parts per million hardness, and in that the water used was aerated to obtain a very high oxygen content. Water used in test ten had a dissolved oxygen content of 9.6 parts per million.

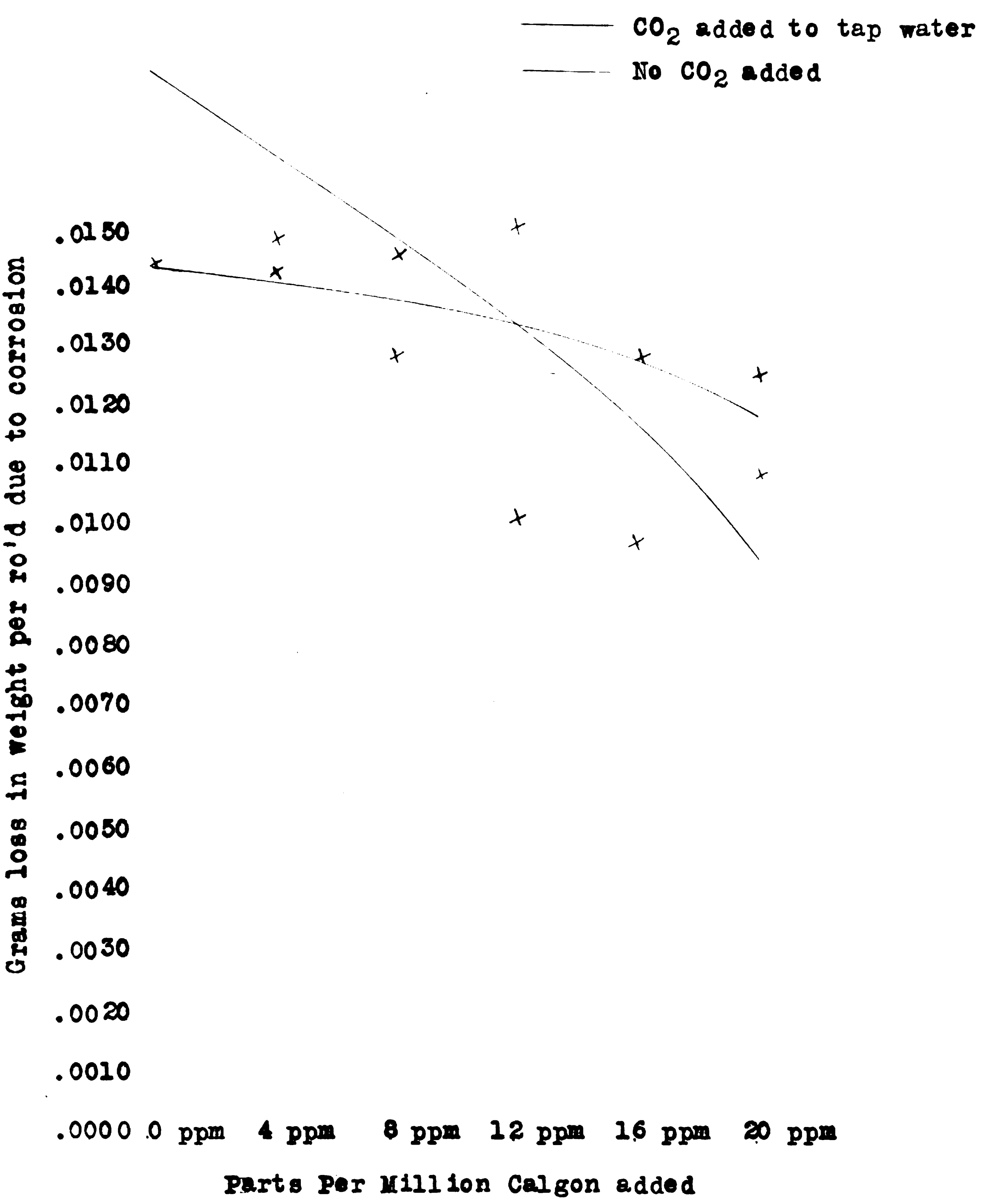
Because of the high oxygen content a very rapid rate of corrosion was obtained, weight losses being higher than in any previous tests. However no appreciable difference in weight losses was observed between bars subjected to water with and water without additions of Calgon. Untreated water caused a weight loss of .0227 grams in bar one, while water treated with 20 parts per million Calgon caused a weight loss of .0201 grams in bar twelve. The slight difference between these weight losses is so small that we must conclude that phosphate glasses have slightly inhibited corrosion in a concentration of 20 parts per million, and are of almost no value at all in lesser strengths.

The value of 23 parts per million hardness of test five was obtained by the use of standard soap solution. A recheck of the soap solution indicates that this value is high, and that the true value is nearer zero. This would show a very close comparison between tests five and ten, both tests showing Calgon to be of little or no value for inhibiting corrosion in zeolite softened waters with very low hardness. However, test six, with a zeolite softened water of 40 parts per million hardness (probably a nearly true value) showed that 20 parts per million Calgon inhibited corrosion to about 55% of the untreated value.

These three tests would indicate that phosphate glasses are of value in inhibiting corrosion when enough calcium is present to give the water a slight hardness, but are of no value in zeolite softened waters of zero hardness or thereabouts.

TEST NUMBER ELEVEN

Curves indicating loss in weight of steel bars with various additions of Calgon (in ppm)



TABULATION OF RESULTS FROM TEST # 11. MICHIGAN STATE COLLEGE TAP WATER WITH HIGH OXYGEN CONTENT. CO_2 CONTENT OF SIX BOTTLES RAISED ABOVE NORMAL VALUE FOR PURPOSE OF COMPARISON. VARIOUS AMOUNTS OF CALGON SOLUTION ADDED TO BOTTLES.

Bottle	Calgon added (ppm)	Rod's loss in weight (grams)	Remarks
1	0	.0142	Aerated only
2	4	.0141	Aerated only
3	8	.0144	Aerated only
4	12	.0101	Aerated only
5	16	.0128	Aerated only
6	20	.0125	Aerated only
7	0	.0189	Aerated and CO_2 added
8	4	.0146	Aerated and CO_2 added
9	8	.0127	Aerated and CO_2 added
10	12	.0148	Aerated and CO_2 added
11	16	.0096	Aerated and CO_2 added
12	20	.0108	Aerated and CO_2 added

Remarks:

All bottles contained water with oxygen content of 9.2

No CO_2 added to bottles 1 through 6, CO_2 content of bottles 7 through 12 increased from normal 26 ppm to 37 ppm

Discussion of Test Number Eleven

Test number eleven is a study to determine the effect of increased CO_2 content upon the aggressiveness of Michigan State College tap water.

Tap water was aerated to raise the oxygen content to a high figure so that the water would be aggressive. Then, to half the bottles CO_2 gas was added from a generating device so that the normal CO_2 content of 26 parts per million of Michigan State College tap water was raised to 37 parts per million.

Various quantities of Calgon were added to both series of six test bottles, concentrations ranging from zero to 20 parts per million in each series. Test rods were then inserted and rotated for a period of 24 hours.

A study of results indicates that the untreated water of bottles seven through twelve with higher CO_2 content was more aggressive than the untreated water of bottles one through six which contained a normal CO_2 content. Calgon seemed to have a greater inhibatory effect upon the water with higher CO_2 content however, so that only a slight variation between rates of corrosion is noted in bottles with a Calgon concentration of 8 or more parts per million.

Results of the test indicate that CO_2 increases the rate of corrosion of untreated water, and that water with high dissolved oxygen content is by nature so aggressive that even the addition of considerable quantities of Calgon had only slight inhibitory effect. Also worthy of note is a comparison between the results of tests ten and eleven, which are in many ways quite comparable with the exception that test ten used softened water while test eleven used tap water. A study of results indicates that the softened water caused far greater losses of weight,and therefore must be considered considerably more aggressive.

TESTS TO STUDY THE EFFECT OF HEXAMETAPHOSPHATE ON THE SOFTENING AND IRON REMOVING CAPACITY OF A ZEOLITE SOFTENER

MODEL ZEOLITE SOFTENER USED IN TESTS

Because of the ability of glassy phospuates to hold Calcium and iron ions in solution some question has been raised as to the effect which adding the chemical to water supplies might have on the ability of zeolite water softeners to remove iron and soften water.

A study of the question seemed to be of value, since the use of phosphates would be most undesirable in localities where zeolite water softeners are used in homes or business places if their use in any interferes with the proper operation of the softeners.

A small water softener was constructed by filling a glass bottle (size 8 inches by 12 inches) with about 3 inches of $\frac{1}{4}$ to $\frac{1}{2}$ inch gravel and six inches of zeolite sand. The volume of zeolite sand in the softener was about 0.2 cubic feet. A siphon arrangement for feeding water to the softener was used so that a constant rate of flow might be obtained. Since water pressure varied greatly in the tap line over each 24 hours period an overflow was added so that water in the siphon feed bottle would be of constant elevation. This arrangement permitted computation of the amount of water passed through the softener and the number of grains of hardness removed between rechargings.

Two series of tests were run in this study. The first series was run over a period of about one and a half months to determine whether the addition of various quantities of Calgon (1 part per million to 50 parts per million) would have any apparent effect upon the operation of the zeolite softener. Two methods of adding Calgon were used in this test. A very low quantity of Calgon was added by the addition of 100 grams of <u>Micromet</u> (a soluble glassy phosphate which dissolves at the rate of 0.8% per day) to the feed bottle so that about 1 gram would go into solution per day, giving a concentration of about 1 part per million. Higher concentrations were obtained by permitting a 1 to 100 solution of Calgon to drip into the siphon bottle at a rate which added the desired concentration (10 to 50 parts per million) of the chemical to water passing through the softener.

In this first series of tests no attempt was made to determine the iron removal in the softener on a quantitative basis. A record was kept of time which the softener was capable of operating with an effluent of low hardness, both with and without the addition of Calgon. The study showed that no apparent difference can be noted between results with treated and untreated water in so far as softening capacity is concerned, the softener being capable of softening water for a period of about

2¼ hours without recharging, the hardness of the water at the end of this time being about 20 parts per million. After 2½ hours time the hardness of the water begins to rise quite rapidly. Results seem to indicate that the addition of glassy phosphates does not interfere with the softening action of a zeolite softener.

Removal of iron by the softener was studied in these first tests by permitting the softener to run for a period of about one week without recharging, and then reversing flow of the water to wash. Michigan State College tap water contains between 0.1 and 0.2 parts per million of iron. The study was made with untreated water, and with waters containing various amounts of glassy phosphate ranging from 1 part per million to 50 parts per million. No apparent difference in results was noted. That is, one weeks operation without washing resulted in the formation of a scum of red iron rust on the surface of the softener, and several minutes washing was required to remove the rust. This scum of iron rust formed with treated and untreated water, regardless of concentration of Calgon used.

These first tests indicated that glassy phosphates do not seem to have any effect on the softening and iron removing capacity of a zeolite softener. It was then felt that a reporting of the actual grains per gallon of hardness removed by the softener with treated and untreated water, and a series of quantitative tests for iron in the influent and effluent of the softener would be of interest.

For the second series of tests all old zeolite sand was removed and new sand added. (Synthetic sand was used in all tests) The softener was then run for several days, no record being kept, and recharging being done whenever the water became quite hard. A test was then run to determine the number of grains of hardness removed during one cycle of operation after recharging. Results are as follows:

Time in Operation	Effluent Hardness (ppm)	Hardness Removed (ppm)
0 hr 10 min	2	348
0 hr 50 min	6	344
1 hr 30 min	12	338
2 hr 5 min	18	332
2 hr 50 min	24	326
3 hr 10 min	69	281
4 hr 30 min	129	221
5 hr 0 min	144	206

Note: Michigan State tap water has about 350 parts per million hardness (as $CaCO_3$)

Next, 100 grams of Micromet was added to the siphon feed bottle, which dissolved at a rate such as to provide one part per million of phosphate for the water passing through the softener. Results are as follows:

Time in Operation	Effluent Hardness (ppm)	Hardness Removed (ppm)
0 hr 10 min	4	346
1 hr 0 min	10	340
1 hr 50 min	14	336
2 hr 30 min	20	330
2 hr 50 min	25	325
3 hr 10 min	30	320
4 hr 30 min	120	230

Finally, 20 grams of Calgon was dissolved in 2 liters of water, making a solution of 1 part per 100 Calgon. This solution was fed into the siphon feed bottle with a glass tube at the rate of 30 drops per minute, providing a concentration of about 50 parts per million to the water passing through the softener. Results were as follows:

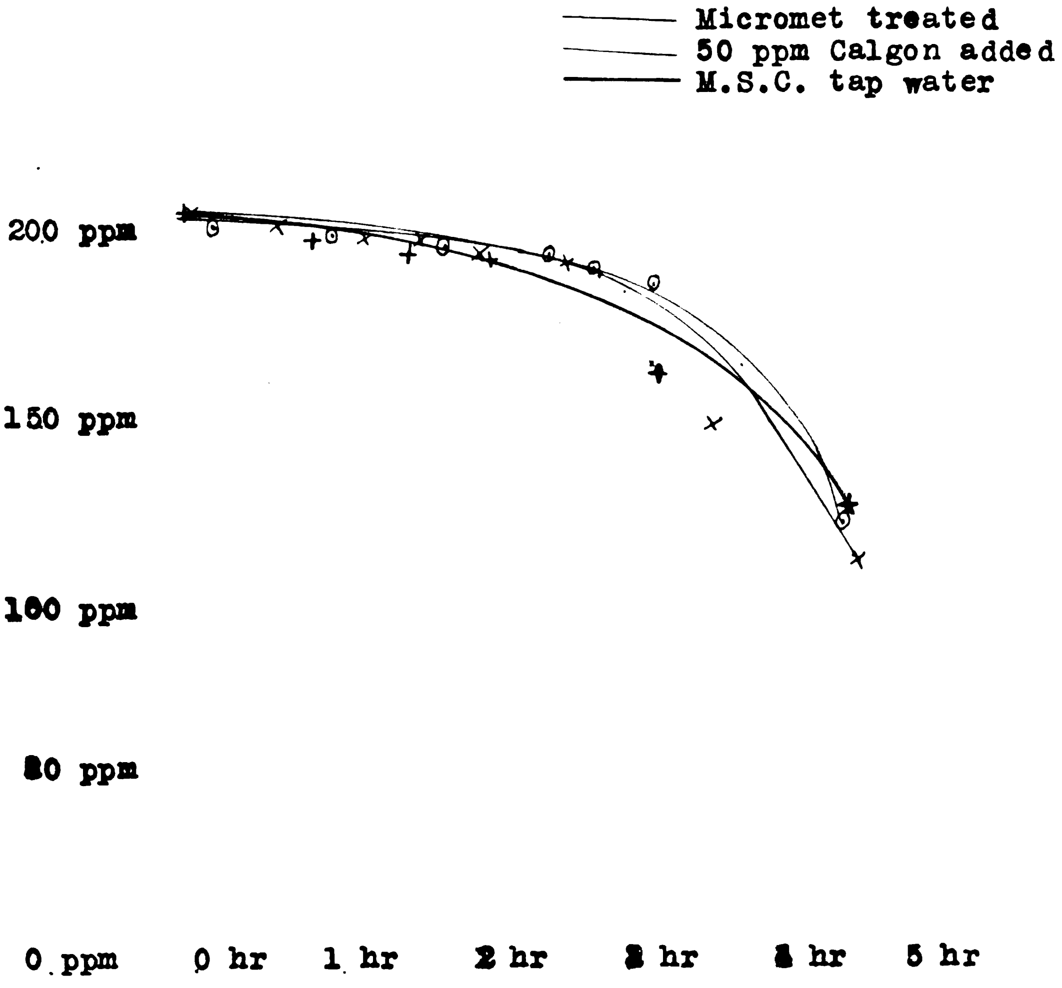
Time in Operation	Effluent Hardness (ppm)	Hardness Removed (ppm)
0 hr 10 min	5	245

Time in Operation	Effluent Hardness (ppm)	Hardness Removed (ppm)
0 hr 30 min	3	347
1 hr 5 min	8	342
1 hr 30 min	10	340
1 hr 55 min	15	335
2 hr 30 min	20	330
3 hr 30 min	80	270
4 hr 25 min	160	190

On the following sheet a plotting of the results from these three tests shows a very close comparison, indicating clearly that Calgon has no effect upon the softening capacity of a zeolite softener when used in such quantities as might be added to a public water system. Since the area under the curves represents total number of grains of hardness removed, the capacity of the softener is about 850 grains(or slightly more if the softener is permitted to become completely discharged). Since the volume is about 0.2 cubic feet of sand, the sand has a capacity of about 4200 grains per cubic foot between rechargings,which is about normal for synthetic zeolite sands.

A quantitative test for iron was run for all of the above tests. Results indicated that all of the 0.2 parts

CURVES SHOWING A PLOTTING OF PARTS PER MILLION HARDNESS REMOVED BY ZEOLITE SOFTENER AGAINST TIME OF OPERATION



Remarks::

Curves show results obtained with tap water, water treated with about one part per million of Micromet and water treated to about fifty parts per million with Calgon per million of iron in Michigan State College tap water was removed by the zeolite softener. That is, an effluent of zero iron content was obtained with raw water and also with all water treated with Calgon. Samples of waters treated with Calgon before softening were boiled to remove any effect of the hexametaphosphate before iron tests were made, and since a result of zero iron content was obtained in all cases it is apparent that the iron was removed by softener, and was not held in solution by the hexamephosphate.

As already stated, these tests seem to indicate that glassy phosphate has no effect upon the softening or iron removing capacity of a zeolite water softener.

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