CORROSION OF MILD STEEL IN ALKALINE SEQUESTERING AGENT SOLUTIONS

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ABSTRACT

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By Thomas Richard Mulvaney

The problem under investigation was the determination of the corrosion inhibiting or accelerating effects of organic sequestering agents, one of the hydroxycarboxylic acid type and one of the aminopolycarboxylic acid type, relative to the effects of the more traditionally used inorganic phosphates and the other components of the system (water, alkali, and hardness-forming salts in water), under conditions similar to those commonly encountered in mechanical washers cleaning reusable glass containers. Review of the literature has indicated a marked deficiency of information on this specific problem and in this general area.

This presentation is divided into two sections. The first deals with the development of experimental procedures and the second with the corrosion investigations. Literature on corrosion testing procedures is reviewed and the results of preliminary tests and tests to obtain suitable procedures for preparing mild steel specimens before exposure and for removal of corrosion products after exposure are included in the first section. The general method employed was that of laboratory total immersion corrosion tests, with the amount and intensity of corrosion determined by weight loss measurement and visual examinations. The second section dealing with the corrosion investigations is divided into five phases of study: (1) Materials and methods, (2) Distilled water-sequestering agent systems, (3) Distilled water-sodium hydroxide-sequestering agent systems, (4) Hard water-sodium hydroxide-sequestering agent systems, and (5) Distilled water and hard water studies combined and compared. Also included in some of these studies are the effects of sequestering agent concentration, temperature, surface-active agent, length of exposure, and successive exposures.

Studies on materials and methods: Corrosion rates of cold rolled and

hot rolled AISI No. C 1008 steel specimens immersed in alkaline sequestering agent solutions did not differ significantly. The experimental procedure developed for these investigations was found satisfactory for use by laboratory personnel having considerable differences in previous training and experience, since results obtained with such personnel did not differ significantly.

Studies on distilled water-sequestering agent systems: Distilled water corrosivity was reduced 97.6 percent with either trisodium phosphate or tetrasodium pyrophosphate and about 75 percent with sodium gluconate (hydroxycarboxylate). Tetrasodium ethylenediaminetetraacetate (aminopolycarboxylate) caused a 12 percent increase in corrosion.

Studies on distilled water-sodium hydroxide-sequestering agent systems: Alkaline solutions of ethylenediaminetetraacetate, gluconate, and pyrophosphate listed in order of decreasing corrosivity were each found significantly more corrosive than the sodium hydroxide control. More corrosion was found at 170°F than at 130°F with the control, gluconate, and ethylenediaminetetraacetate solutions. The addition of a surface-active agent to gluconate solutions did not significantly alter the solutions' corrosivity. The amount of corrosion found with one, three, five, and seven day exposures did not differ significantly except with ethylenediaminetetraacetate.

Studies on hard water-sodium hydroxide-sequestering agent systems: The gluconate solutions were markedly more corrosive than the control, which was itself significantly more corrosive than pyrophosphate, ethylenediaminetetraacetate and orthophosphate, which themselves did not differ significantly in corrosivity.

Distilled water and hard water studies combined and compared: Distilled water plus ethylenediaminetetraacetate was significantly more corrosive than distilled water, which was itself significantly more corrosive than 12 grain per gallon hard water. Corrosion rates of alkaline hard water solutions of gluconate and of the control were significantly greater than their distilled water counterparts. Corrosion weight loss was found to increase slightly as the concentration of ethylenediaminetetraacetate was increased from one-to-two-to-four moles of sequestrant per mole of alkaline earth metal cations in alkaline distilled water solutions, but not in alkaline hard water solutions. The corrosion weight loss of mild steel specimens was found to increase linearly with gluconate concentration over the same range in alkaline distilled water solutions according to the following calculated predicting equation:

$$\hat{Y} = 3.065 + 2.601X$$

Corrosion weight loss with gluconate in alkaline hard water solutions over the same concentration range was found to decrease linearly as a function of concentration when the logarithm of weight loss was plotted versus the reciprocal of concentration, thus giving the following calculated predicting equation:

$$\log \hat{Y} = 0.7782 + \frac{0.006442}{X}$$

The apparent discrepancy between the effects of sodium gluconate concentration on corrosion in these distilled water and hard water solutions may be explained as follows: In the first case gluconate anions are free to sequester ferrous ions of the ferrous hydroxide protective film of corrosion products, and as the concentration of gluconate is increased more ferrous ions can be sequestered. As the film is diminished in such a manner, less resistance is afforded to the diffusion of oxygen to the cathodes, and corrosion is thereby promoted. In the second case alkaline earth metal cations are present in solution and the gluconate anions would normally be expected to sequester them, thus forming a stable water soluble complex. However it is proposed that possibly the complex so formed is not adequately solubilized at the lower concentration and that intermingling of this complex with the corrosion products could decrease their protectivity and result in increased corrosion. Addition of more gluconate could enhance the solubility of the complex leaving less to alter the corrosion products protectivity. As a result less corrosion might be found with increasing gluconate concentration.

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INTRODUCTION

Scale in beverage bottle washers results in interference with normal bottle pickup and release, increased carry over of washing solutions into the rinse sections of the washer, increased wear and drag of moving parts, decreased speed of machine operation, and impedance of heat transfer due to layers of scale on the heat transfer surfaces. To obtain clean beverage bottles, and for efficient and effective bottle washer operation, scale formation and accumulation in the washer and on its moving parts must be prevented.

The beverage industry usually softens the water used for cleaning reusable containers by chemical treatment. Sequestering agents of both the inorganic and organic types are utilized for this purpose. The most widely used sequestering agents are the inorganic phosphates because of their relatively low cost. More recently the organic complexing agents such as the alkali metal salts of the hydroxycarboxylic acids (e. g., sodium gluconate) and the aminopolycarboxylic acids (e. g., tetrasodium ethylenediaminetetraacetate) have become increasingly more important in beverage bottle washing. With the increased use of sequestering agents, concern relative to the effect of these agents on the washing machine has developed.

A difference of opinion exists in the beverage industries as to the effect of these agents on bottle washing equipment. Information on the corrosiveness of these agents is needed and would be of value to the various beverage industries and their suppliers. This investigation was designed to examine the corrosion characteristics of basic chemical ingredients that are used either singly or in formulated compounds so as to better understand the behavior of these compounds under bottle washing conditions. No formulated bottle washing detergent compounds or mixes were examined since the effect of individual ingredients could not be determined. This investigation is a part of a project sponsored by the American Bottlers of Carbonated Beverages Association to evaluate the effect of basic bottle washing components on washing equipment and their effectiveness in cleaning soiled bottles, to ultimately ascertain if present standards for cleaning carbonated beverage bottles are satisfactory or if they should be revised.

This thesis describes the results of an investigation of the corrosion of mild steel in alkaline sequestering agent solutions. The first part of this thesis describes the development of the experimental procedure employed in the investigation. Literature on corrosion testing procedures is reviewed and the results of preliminary tests to obtain suitable procedures for preparing specimens before exposure and removing corrosion products after exposure are included. The second part of this thesis describes the results of the investigation to determine the effect of organic and inorganic sequestering agents on the corrosion of mild steel in distilled water, distilled water plus sodium hydroxide, and hard water plus sodium hydroxide solutions under a variety of test conditions.

REVIEW OF LITERATURE

Corrosion Costs

Estimates have been made of the economic cost of corrosion. Uhlig (1949) made a careful survey of only the direct losses by corrosion in the United States and reported a rate in excess of $5.5 billion annually. Jelinek (1958) states that in the nine year interval since Uhlig's study was published, corrosion control methods have improved considerably, but material and labor costs have generally risen and thus the order of magnitude of the direct costs of corrosion remains about the same. Schmitt (1960) states that corrosion problems cost near $8 billion annually, while mining metals cost about $1 billion annually. Gegner (1960) says that the cost of corrosion to this country has been estimated by various experts to be upwards of $7.5 billion per year of which industry's share is about $6 billion. Included in these estimates are the direct costs due to corrosion alone; such as replacement and maintenance of corroded equipment, costs of painting, electroplating, and other protective measures including application and labor costs. Among the indirect costs not included are such things as safety hazards, product contamination, shutdown time and loss of products when equipment fails. Equipment overdesign is often required where uncertainty relative to corrosion effects exists. Thus, it is readily apparent that strong incentives exist for improvement in decreasing corrosion. Improvement of only one percent in decreased corrosion would mean an annual savings of at least $55 million. Another example of the tremendous cost of corrosion, which in this case should be of particular interest to the American automobile owner follows: It has been reported in a staff feature of Corrosion (1961) that corrosion damage to automobile exhaust systems cost American car owners over $500 million in 1960. According to this report, 30 million mufflers sold in 1960 at an average retail price of $12.50 for a total of $375 million. About 35 million tailpipes were also sold the same year at an average retail price of $5 for a total of $175 million, giving a grand total of over $500 million. It was pointed out that the loss to corrosion of auto mufflers alone ($375 million) equaled the total cost to the United States for construction of the Panama Canal.

Gegner (1960) states in his paper on alkaline environment corrosion that industry has long been experiencing a steady erosion of its profits. Further, that competition, public opinion and more recently a genuine fear of inflation has prevented most of them from raising prices to maintain their margin of profit and thus industry has been forced to search out every possible means for reducing its manufacturing costs. He goes on to point out that because of its size, maintenance cost is one of the obvious targets and within this area are the sizeable costs attributable to corrosion.

It is this same concern relative to maintenance and replacement costs within the carbonated beverage industry which is the primary reason for this study. The specific problem pertains to the corrosive effect of relatively recently introduced sequestering agents on the bottle washer, relative to the corrosive effects of the more traditionally used agents and components of the cleaning systems.

Corrosion of Iron and Steel

Nieland, Maguire, George and Kahler (1950_a) have reported that soluble salts of hydroxypolycarboxylic acids having less than 7 carbon atoms, such as sodium citrate, tartrate, malate, and mucate form a visibly thick, black, tenacious film over iron surfaces. Concentrations from 0.1 to about 100 ppm reportedly gave maximum protection; higher concentrations decreased protection and caused pitting. Above 1000 ppm the total weight loss of the exposed specimens exceeded that of the control. Sodium citrate was reported to have penetrated existing tuberculation products and to have formed a film on the base metal underneath, gradually restoring the carrying capacity of pipe. They found 2 ppm of sodium citrate to give 60% protection in Philadelphia tap water at 160°F, which was noted as being triple the protection of 2 ppm of sodium hexametaphosphate, or 100 ppm of sodium silicate solution (28% SiO_2). The film was reported as seeming to be established in all cases in about 5 days. It was pointed out that the film with sodium citrate formed fastest in low hardness water. The greatest corrosivity was found in intermediate hardness waters.

Nieland, Maguire, George and Kahler (1950_b) have also reported that solutions of 0.1 to 100 ppm of sodium gluconate and gluconic acid act similarly to other hydroxycarboxylates and form a hard, dark, corrosion resistant protective film over iron surfaces. Above 100 ppm the over-all protection was found to continue without appreciable reduction in weight loss, but the attack localized in pits, and perforations were found in a flow system using Philadelphia tap water of 42 ppm total hardness as $CaCO_3$ at 120°F. The percent protection given for a concentration of 840 ppm of sodium gluconate was about 84%. It was stated that sodium gluconate penetrates existing corrosion products, forming a film on the metal underneath and allows for their gradual removal. It was found that the dosage could be reduced once the film was formed.

Dvorkovitz and Hawley (1952_a) have stated that hard adherent scale or etchings formed on glassware from the constituents of water in which it is washed, is inhibited by the use of a mixture of about 90 parts by weight of caustic alkali, such as sodium hydroxide, and 10 parts of sodium or potassium gluconate. They noted that this mixture also serves as a better inhibitor of rust, and iron and steel corrosion, than sodium hydroxide solutions alone.

Dvorkovitz and Hawley (1952_b) have also stated that the hard water used for rinsing glass, metal, rubber, and porcelain articles coming from alkaline washing solutions can be treated with caustic alkali and alkali metal gluconates in the amounts of 0.25 - 20% and 0.025 - 2.0%, respectively. This treatment is advocated in order to prevent or reduce scale precipitation of calcium and magnesium salts which interferes with the clearing operation on the surface of the objects. It was pointed out that such solutions have the advantage of better inhibition of rust and corrosion of iron and steel, and are relatively non-foaming.

An extract of a 1955 letter from Glyco Products Company forwarded to us by Cooper (1960) of the George J. Meyer Manufacturing Company, states, "it is reported that corrosion of washing equipment occurs with sodium gluconate compositions. In addition, this type of compound does not sequester iron or aluminum. Aluminum is deposited in washing from aluminum labels frequently used on milk bottles."

Shaw and McCallion (1959) have reported results on corrosion by gluconate-caustic systems and other considerations. They stated that, "some time ago corrosion of bottle washing equipment using gluconate-caustic solutions was reported. Actually the complaints were not widespread but the fact that they existed at all, was sufficient reason to begin an investigation." The experimental procedure employed will be described in detail in the development of experimental procedure section of this dissertation. The type of metal (carburized and hardened steel), pre-cleaning procedures and procedures for the removal of corrosion products differed from those employed in the subsequent studies to be reported here. Duplicate tests were conducted with rotating specimens. Test solutions of 3% caustic plus additives (based on total solution weight) were prepared using water of 12 grains per gallon hardness. Each test was conducted for 7 days in a constant temperature bath at 140°F. The results as reported in mils penetration per year (MPY) and recalculated (metal density assumed = 7.87 gm/cm^3) to give the results in terms of weight loss (mg/dm^2-week) are given in Table 1. They noted that test solutions containing phosphates were generally not as corrosive as the gluconate-caustic system, and in fact reduced corrosion to a point much less than the caustic control. When the level of gluconate was reduced from 0.15% (which is three times as much as is theoretically required for 12 grain hardness water) to 0.045% (mole to mole with calcium) the corrosion rate was reduced 60% to a point essentially the same as that of the caustic control. They stated that, "the corrosion results certainly indicate that the higher the level of gluconate, the more corrosion. The primary lesson, therefore, is that large excesses of gluconate should be avoided. Large excesses are quantities far over and above the levels actually required to do a satisfactory job." Shaw and McCallion present recommendations as to amounts of gluconate to be used, based on the fact that 1 mole of gluconate sequesters 1 mole of calcium or magnesium. The gluconate levels recommended in practice are twice these amounts. It was also pointed out that the gluconate level may need to be still higher if rusty necks, aluminum labels, bottles containing cement, etc., are common occurrences.

Cooper (1960) states that as a result of non-biased laboratory and field investigations on sodium gluconate and other sugar acid materials,

Table 1. Corrosiveness of some gluconate-caustic systems (Shaw and McCallion (1959)).

Test solutions	Corrosion rate	
	Mils penetration per year, MPY	Weight loss, mg/dm^2-week
3% Sodium hydroxide	0.40	15.38
3% Sodium hydroxide + 0.15% sodium gluconate	1.11	42.67
3% Sodium hydroxide + 0.045% sodium gluconate	0.47	18.07
3% Sodium hydroxide + 0.10% sodium gluconate + 0.10% trisodium phosphate	0.21	8.07
3% Sodium hydroxide + 0.15% sodium gluconate + 0.05% trisodium phosphate	0.24	9.23
3% Sodium hydroxide + 0.10% sodium gluconate + 0.10% sodium tripolyphosphate	0.05	1.92
3% Sodium hydroxide + 0.15% sodium gluconate +0.0075% sodium tripolyphosphate	0.54	20.76
3% Sodium hydroxide + 0.10% sodium gluconate + 0.10% sodium hexametaphosphate	0.09	3.46
3% Sodium hydroxide + 0.10% sodium gluconate + 0.10% tetrasodium pyrophosphate	1.45	55.74
3% Sodium hydroxide + 0.15% sodium gluconate + 0.05% Renex (surface-active agent)	0.72	27.68

that they do not recommend the use of these materials in Meyer Dumore washers. He points out that it is true that these compounds, if properly used, will inhibit scale formation in the strongly alkaline compartments of the washing machine; however, he also points out that if the materials are used they must be carefully tailored to fit the conditions in each bottling plant. He states that too much of the gluconate will favor rusting and too little will not give the proper amount of protection. He goes on to point out that even if the proper amount of material is added to the freshly prepared solution, there is no method known for the rapid evaluation of the residual gluconate, in order to bring up the percent of material to the original working strength. Cooper states that they have information from a manufacturer of gluconates stating that as the caustic strength decreases in the various washer compartments, the efficiency of gluconate drops rapidly to the point where it gives no protection. They advocate the use of some material such as tetrasodium pyrophosphate in the rinsing compartment of the washer in order to prevent scale build up.

White (1962) points out that it is undesirable to go significantly beyond the minimum concentrations and temperatures recommended for washing bottles because hot caustic solutions are very corrosive to the machine and to the glass itself.

Putilova, Balezin, Barannik (1960), and Levina (1956) state that the solution of iron in alkalies has received relatively little study. They note that various substances have been used as inhibitors of the solution of iron in acids. Among these are the substituted aliphatic and aromatic amines, sulfonated naphthalene and anthraquinone derivatives. These inhibitors are reported to be quite ineffective in alkaline solutions, since they are not adsorbed on the iron under these conditions. This has been attributed by Levina to the fact that some are practically insoluble in alkaline solutions, and also to the fact that iron in alkaline solution is coated by oxides that have very pronounced hydrophilic properties. For these reasons the author stated that the choice of inhibitors of iron corrosion in alkaline media should differ from those used for acid solution. Levina states further that the addition of substances capable of forming surface compounds with iron and its oxides should prove to be inhibitors of the solution of iron in alkaline solutions. To determine if such was the case, silicic acid, sodium phosphate, and tannin were chosen to be evaluated. These substances were noted as being easily soluble in alkalies and also to form stable chemical compounds with iron and its oxides. Levina states that it was not possible to predict their influence on the solution of iron. The data obtained in the studies showed that silica gel, phosphate, and tannin form surface compounds with the iron. It was reported that these compounds retard solution of iron by raising the hydrogen overvoltage and that this is not accompanied by a decrease of the electrochemical activity of the iron surface. Electrodes treated in this manner were shown to have considerable electrochemical capacity. It was further noted that when large quantities of these inhibitors were added, gas evolution at the iron ceases and the iron loses its electrochemical activity.

Corrosion of Some Other Metals

McCune (1958) investigated and reported on corrosion of aluminum by alkaline sequestering solutions. Corrosion of aluminum by solutions of sodium triphosphate and sodium ethylenediaminetetraacetate (sodium ((ethylenedinitrilo)) tetraacetate) is treated in detail. Weight loss data were determined with an analytical balance on specimens exposed in stagnant total immersion tests. The ratio of area of metal to volume of solution used was 29 cm^2 per 200 ml. Aeration was shown not to affect the results appreciably. Distilled water and reagent grade chemicals were used in preparing the test solutions. Solutions of sequestering agent (sodium ethylenediaminetetraacetate, pyrophosphate, triphosphate) corroded aluminum much more rapidly at 60°C than solutions of non-sequestering salts (sodium trimetaphosphate, sodium sulphate, tetramethylammonium sulphate) at alkaline pH values up to about 10.5. Above this pH, alkaline corrosion reportedly overwhelmed sequestering corrosion. The data were obtained at constant pH. With sodium triphosphate corrosion was general over the surface of the metal and conditions of 60°C, 3 hours, and 200 ml of 0.18% sodium triphosphate solution resulted in etching and a decrease of specular reflectivity of the metal with little or no discoloration. Lower sodium triphosphate concentration, smaller volumes, and longer times caused a brown discoloration. Pitting was not observed at the pH of sodium triphosphate solutions. In the presence of sufficient sodium triphosphate, aluminum perchlorate-perchloric acid solutions were found to form no precipitate when sodium hydroxide was added between pH 3 and 11. The over-all reaction was reported to be that of metallic aluminum with triphosphate solution to give an aluminum-triphosphate complex and hydrogen, and in the pH range 7 to 10, hydroxide ion. The following overall reactions were indicated as illustrative: At about pH 8;

$$Al + 3H_2O + HP_3O_{10}^{-4} = (Al(OH)_2HP_3O_{10})^{-3} + OH^- + 1.5H_2$$

At about pH 10;

$$Al + P_3O_{10}^{-5} + 3H_2O = Al(OH)_3P_3O_{10}^{-5} + 1.5\ H_2$$

It was reported also that aluminum immersed in 0.18% phosphorus -32- tagged (P^{32}), sodium triphosphate solution for 3 hours at 60°C sorbed phosphate equivalent to 0.019 mg sodium triphosphate per cm^2, according to radioactive count. McCune stated that the action was apparently in the hydrous oxide surface film, since the radioactive triphosphate was removed by the nitric acid rinse which dissolves corrosion products, but very little of the metal itself. The surface film isolated from an aluminum foil exposed to 0.18% of sodium ethylenediaminetetraacetate solution under the same conditions contained nitrogen and carbon indicating the presence of the sequestrant in the film. The over-all corrosion reaction at about pH 8.5 was given as

$$Al + 2H_2O + HEDTA^{---} = (Al(OH)EDTA)^{--} + OH^{-} + 1.5\ H_2$$

It was further pointed out, that this demonstration of the presence of the corrosive agent at the solid surface is pertinent to recent discussion of chelating agents as corrosion inhibitors or as corrosion accelerators in cases where the surface complex of the chelating agent and metal ion is sufficiently stable to disrupt the metal or oxide lattice. Additions of metal cations to triphosphate solutions were found to reduce corrosion; the order of increasing effectiveness was found to be the same as the order of increasing complexing strength of these cations by the polyphosphate. Lithium, calcium and magnesium, and aluminum and nickel sulfates reduced the corrosiveness of sodium triphosphate, with effectiveness increasing in that order.

Sundararajan and Char (1961) studied the corrosion rates of commercial aluminum, containing 4 percent manganese and 3 percent iron, in sodium hydroxide solutions under different conditions. Inhibitor efficiencies were calculated for the following substances, the efficiency decreased from 90 to 60 percent in the order: agar-agar, gum-acaciae, dextrin, gelatin, and glue. Corrosion potentials were measured with and without dextrin inhibitor, and cathodic and anodic polarization studies were also made. They reported that the results obtained showed that the dissolution of the metal was electrochemical in character. The corrosion process was described as appearing to be under mixed control, with the predominance of action of dextrin inhibitor on the anodic areas of the metal surface.

Moore and Smith (1942) conducted laboratory studies to determine the influence of metaphosphate on the quantity of lead picked up by water passing through lead wool and through lead pipe previously exposed to corrosive water. They reported that in water having a pH value of 7.0 or less, the addition of metaphosphate materially reduced the amount of lead taken up by the water. It was reported that under certain conditions, the addition of metaphosphate to a water having a pH value of 8.8 resulted in an increased amount of lead taken up by the water. (The authors pointed out that it seemed to them that the gravest question (with regard to danger to public health) with respect to the introduction of metaphosphate into water systems containing lead pipe was the effect of this chemical on the deposits of lead salts previously formed in the pipe.) They stated that most recent work indicates that metaphosphate treatment is most effective at low pH values.

Jensen and Claybaugh (1951) reported on the corrosive effects of sodium tripolyphosphate and tetrasodium ethylenediaminetetraacetate on tinned steel when used as 90% of detergent in 0.3% distilled water solution and in presence of 0, 4, 8, 12, 16, 20, 24, and 36% sodium metasilicate with a five day exposure period. Weight losses of 0.1462 g and 0.2884 g were reported for sodium tripolyphosphate and tetrasodium ethylenediaminetetraacetate respectively, when no sodium metasilicate was added to the solutions. Addition of 0.4% metasilicate to the tripolyphosphate solution reduced the weight loss to 0.0084 g. Additional corrosion inhibition was not particularly apparent above this level of metasilicate. The addition of metasilicate in amounts up to 24% did not prevent tetrasodium ethylenediaminetetraacetate's heavy corrosion.

Lewandowski (1952) presents comparative data on some acids used in dairy cleaning. The study included corrosion of tin plate (hot-dip and electroplated tinned steel strips were both used) and stainless steel (18-8 sheet) strips in sodium bisulfate and in phosphoric, gluconic, levulinic, glycolic, citric, acetic and sulfamic acids. All acidic solutions were prepared in distilled water with a final concentration of 0.25 percent by weight. The strips (about 3 x 1 in.) were precleaned before partial immersion in essentially static test solutions (70 ml). After immersion the cleaning procedure consisted of rinsing the strips three times in distilled water, with light brushing during the second rinse. The strips were then dried and weighed. Lewandowski concluded that factors contributing to corrosion of tinned steel by mild acidic solutions were temperature, pH, apparent volatility of organic acids, structure of acidic compounds and type of tinplate. Weight loss of tinned steel changed or remained constant with change in temperature depending on the acid compound and type of tinplate. Under all test conditions, phosphoric acid caused only very slight weight losses as compared to the various organic acids, and sodium bisulfate and sulfamic acid. Lewandowski noted that the corrosion weight loss figures obtained were all below the so called "serious" weight losses represented by 100 mg/dm^2-day, which he points out is an indication of the essentially mild nature of all the tested acidic solutions. An apparent relationship between pH of acidic solutions and formation of colored deposits, as well as spangling (seemingly etched patterns) of treated tinned steel strips was observed. Pitting of tinned steel was observed only with volatile organic acids, and was also related to the presence of sulfur in molecules of the inorganic acidic compounds used. Corrosion was noted as more intense on thinly electroplated than on heavily plated hot-dip steel. Stainless steel was not appreciably corroded by any of the acidic solutions tested.

Solutions of four polyphosphates (tetrasodium pyrophosphate, sodium tetraphosphate, sodium hexametaphosphate, and sodium tripolyphosphate) were shown by Bacon and Nutting (1952) to dissolve copper, zinc, or brass. Corrosion rate data were presented for several metal-polyphosphate combinations at 80°C and for several commercial and experimental dishwashing detergents. The inclusion of sodium metasilicate was shown to afford a practical means of retarding the corrosive action of polyphosphates on dishwashing machine parts. Of the several polyphosphates investigated, pyrophosphate was the most difficult to inhibit. It was pointed out that corrosion of copper, brass, or bronze pumps, valves, and spray nozzles by polyphosphated detergents may seriously reduce the efficiency of dishwashing machines and that many complete failures of machine parts have occurred within 6 months. A brassy tarnishing of silverware washed in certain dishwashing machines was attributed to copper solubilized from machine parts by poorly inhibited polyphosphated detergents that then plated on the silverware by electrolytic action.

Getty, McCready, and Stericker (1955), have determined the degree of corrosion with some synthetic detergent solutions (wetting agent plus polyphosphate), and the degree of protection obtained by the addition of various amounts of various silicates. The tests were made with aluminum, zinc, copper, brass, nickel silver, and several enamels. The addition of certain sodium silicates reduced corrosion or tarnishing of the metals in household detergent mixtures containing polyphosphates. It was pointed out that the silicate content of the most popular heavy-duty household detergents now on the market is sufficient to prevent the corrosion of aluminum, but an increase would be desirable to reduce corrosion of zinc and its alloys. It was shown that silicated detergents lessen any attack and loss of gloss of enamels, and especially with less resistant enamels.

Wright (1956) has also reported that silicates are effective corrosion inhibitors for cleansers of aluminum dairy equipment (particularly aluminum milk cans).

Hunziker, Cordes, and Nissen (1929) studied the resistance to corrosion of 19 different metals, plated metals, and metallic alloys in solutions of washing powders, chemical sterilizers, and refrigerating brines. The metals included in the tests were: manganese-aluminum alloys, aluminum plated alloy, copper, nickel, monel metal, nickel silver, tin, tinned copper, tinned iron, iron, zinc, galvanized iron, ordinary chromium steels in the form of Ascoloy and Enduro, and a chromium-nickel steel in the form of Allegheny Metal. The alkalies tested were a special alkali (35% NaOH, 62% Na_2CO_3), sodium carbonate, Wyandotte (49% Na_2CO_3, 36% $NaHCO_3$), sodium hydroxide, trisodium phosphate, and commercially formulated tin cleaner, and Diversol. Chemical sterilizers were sodium hypochlorite, Diversol, and Chloramine-T. The test comprised partial immersion of the metal strips in solutions in closed Mason jars for 5 hours at 150°F for alkalies and 5 days at 70°F for chemical sterilizers. Hunziker, Cordes and Nissen used 0.5 percent solutions of alkalies. Aluminum products suffered by far the most intense corrosion in all washing solutions used. The tinned copper and tinned iron products ranked next in intensity of corrosion, but showed much greater resistance than the aluminum products. Of the remaining metals, the corrosion of copper, iron, galvanized iron, and zinc was decidedly greater, but not as severe as that of the tin-plated products. They found that the addition of 0.025 percent sodium chromate to 0.5 percent solution of trisodium phosphate in water very greatly reduced corrosion. With 0.5 percent solutions of alkalies, the addition of sodium silicate in 0.05 percent quantities did not reduce the attack of NaOH and trisodium phosphate, but completely eliminated corrosion by soda ash. The use of trisodium phosphate solution (0.16 to 0.5 percent) combined with 0.025 percent sodium chromate was described as best from the corrosion standpoint for tin-coated equipment.

Parker (1942) reported a laboratory study of the corrosive action of an acid cleansing product known as Mikro-San (described as being a non-toxic mixture of certain organic acids, specific wetting agents, corrosion inhibitor, and a microstatic agent), and acid sterilizing product known as Mikro-Puer (content not given), and Chicago tap water on nine different metals normally used in the construction of can washers and dairy processing equipment, as well as that used in the construction of milk cans. The results obtained were compared with those of Hunziker, Cordes, and Nissen (1929) described above. Parker concluded that the corrosive effects of Mikro-San, Mikro-Puer and Chicago tap water were relatively mild compared to the various mineral and organic acids, and particularly to the action of the various washing powder solutions used by Hunziker, Cordes and Nissen.

deVleeschauwer, Hendrickx, and Moulaert (1951) investigated the influence of several detergents on aluminum, tinned iron, tinned copper, yellow and red copper, galvanized iron, and chromium-plated red copper. Cleaned metal plates were weighed and immersed for three consecutive 24 hour periods in 70°C detergent or immersed for three consecutive 5 day periods in 20°C disinfectant. The plates were rinsed, visually examined, dried, weighed and placed in new solution after each immersion. The weight loss data were used to determine the resistance to corrosion of the metals. They stated that aluminum was generally the most affected.

Corrosion of the tinned iron and tinned copper were noted as not particularly important, but corrosion was observed with each solution tested. Weight losses from the yellow and red copper specimens were noted as being small, but they were stained and made dark by most of the detergents. It was observed that some products did not affect galvanized iron while others affected it strongly. Chromium-plated red copper was only affected by Trosilin, and stainless steel was not affected at all by any of the detergents. A 0.5% solution of a quaternary ammonium compound was reported to have affected only the tinned metals, yellow and red copper, and galvanized iron. Sodium hypochlorite solution of 120 ppm affected aluminum; a higher concentration affected tinned metals, but to a lesser extent. Solutions of only 15 ppm were said to have stained copper and galvanized iron. The disinfectant solutions were found not to affect chromium-plated red copper and stainless steel.

deVleeschauwer, Hendrickx, and Wallez (1953) studied the corrosive effect of detergents on milk-can metals. Aluminum and tinned iron were tested in solutions containing sodium hydroxide, sodium carbonate, sodium phosphate, sodium silicate and sodium hexametaphosphate. In the immersion test method used, each test panel was given 180 immersions of 1 minute each, rinsed, dried, and weighed. They noted that weight losses of light metals in milk-can cleaners should not exceed 20 g/m^2-day and 60 g/m^2-day for heavy metals.

Haller, Grant, and Babcock (1941) studied the corrosive action of what they described as typical chlorine disinfectants for use on dairy equipment under various conditions. It was determined that sodium hypochlorite and Chloramine-T solutions containing approximately 200 ppm of available chlorine would corrode most metals used in the dairy industry.

Other studies on the effects of washing media on metals other than iron and steel, are those of Bablik and Belohlavy (1957), Stupel and Kock (1959), and Bukowiecki (1958). Bablik and Belohlavy investigated and determined that certain detergents containing polyphosphates will attack hot galvanized surfaces. Stupel and Kock determined the corrosive effects of some soaps and washing compounds on stainless steel, copper, brass, bronz, tin, zinc and aluminum. Bukowiecki investigated the effects of various detergents on metals used in the construction of washing machines. The materials tested included galvanized steel, copper with and without a solder or tin deposit, and aluminum alloy, and brass. Sheet metal samples were suspended in solution at 90°C and the weight loss determined every three hours. The effects of agitation, water hardness, and contact between dissimilar metals were investigated. The most intensive attack was found to be produced by the simultaneous action of polymerized phosphates and sodium perborate. Soap had little effect and it was stated that it may even act as an inhibitor. Galvanized steel and the aluminum alloy were found most susceptible to corrosion by detergents. Stainless steel and nickel-plated copped alloys were described as virtually corrosion resistant. It was also observed in some instances that interaction of two metals led to anodic inhibition.

It is apparent from the literature that many investigations have been conducted in the general area of detergent corrosion of metals and alloys. However the effect of alkaline sequestering agents on the corrosion of mild steel have not been determined. Further there is a need for a comprehensive evaluation of the corrosive effects of organic sequestering agents, relative to the effects of the more traditionally used inorganic phosphates and other components of the systems, under conditions similar to and varied in accordance with what is commonly encountered in their practical use. General aspects pertaining to sequestering agents and their chemical behavior are elaborated in the next section.

SEQUESTERING AGENTS AND THEIR CHEMICAL BEHAVIOR

Sequestering agents are used to chemically soften hard water used in cleaning reusable glass containers. The basic bottle washing recommendation of the "American Bottlers of Carbonated Beverage Association" (1958) is: "unclean bottles shall be exposed to a 3 percent alkali solution of which not less than 60 percent is caustic (sodium hydroxide), for a period of not less than 5 minutes at a temperature of not less than 130°F, or to an equivalent cleansing and sterilizing process." The bottles are then rinsed free of washing solution. Of the 43 states having requirements governing type and strength of solution, 26 of them follow this recommendation very closely, allowing only one solution concentration, a minimum temperature, and a minimum contact time. In addition to the alkali used, other agents may be added to either improve solution detergency or for chemical water-softening purposes, since the sodium hydroxide bottle-washing solutions are adversely affected by hard water salts. The high hydroxyl ion concentration tends to precipitate metal ions as slightly soluble hydroxides. Chaberek and Martell (1959) demonstrate the low solubilities of the calcium and magnesium salts of the anions present in these washing solutions by the following table:

Table 2. Solubilities of some calcium and magnesium salts in water.

Anion	Solubility, g/1	
	Calcium	Magnesium
Carbonate	0.014	0.1
Hydroxide	1.85	0.009
Phosphate	0.02	0.2
Silicate	0.09	---

They point out that this leads to serious precipitation problems, which result in both improper cleaning of the glass containers and acceleration of scale formation on the washing machine. Skaggs and Miller (1958) concur with this as pointed out in their studies of the influence of hard water on dairy detergents.

Chemical water treatment is most commonly followed in dealing with the water-hardness problem in bottle washing solutions. The softening agent, hereafter referred to as a sequestering agent, is added when unformulated mixes are used at the time of making up the solutions or when they are added to the washer. It is appropriate at this point to define sequestration and other terms in this area.

Smith (1959) summarizes what is meant by sequestration and defines what function a material must perform to be regarded as a sequestering agent. He states,"sequestration consists in the suppression of a particular property or properties of a metal in solution, without the removal of that metal either into another phase nor its concentration into a particular portion of the original phase, while at the same time the agent used for the purpose of this sequestration must not introduce any new factor, reaction, or characteristic which makes the system unsuitable for the original purpose."

Chaberek and Martell (1959) state that a metal complex or metal coordination compound is the resulting substance when water molecules surrounding a metal ion are replaced by other molecules or ions. The group which combines with the metal ion is called a ligand. A metal chelate compound (or metal chelate) is defined simply as a complex in which the donor atoms (the atoms directly attached to the metal) are attached to each other as well as to the metal and the metal becomes part of a heterocylic ring. When a ligand forms a stable, water-soluble metal chelate or metal complex, the ligand is said to be a sequestering agent and the metal is said to be sequestered. The ligand (donor molecule or ion) of a stable, non-water-soluble metal chelate or metal complex may be referred to as a precipitating agent and the metal is said to be precipitated.

Agents used for chemical water treatment may be classed as inorganic and organic agents, examples of which follow: Trisodium phosphate is an inorganic water-softening agent, softening by precipitation. Tetrasodium pyrophosphate is also an inorganic water-softening agent, softening by sequesteration. Two groups of organic sequestering agents of importance are the hydroxycarboxylic acids such as gluconic acid and the aminopolycarboxylic acids such as ethylenediaminetetraacetic acid. Chaberek and Martell (1959) point out that the most widely used sequestering agents are the inorganic polyphosphates (pyrophosphates, tripolyphosphates, and polymetaphosphates), because of their relatively low cost. In recent years the organic sequestering agents have become increasingly important. The organic sequestering agents and their compounds have higher thermal stabilities and tend to resist the effects of prolonged exposure to high temperature and alkalinity, while the polyphosphates tend to hydrolyze back to trisodium phosphate under these conditions.

The sequestering agents to be used in this study are trisodium phosphate (not technically a sequestering agent), tetrasodium pyrophosphate, sodium gluconate, and tetrasodium ethylenediaminetetraacetate. Trisodium phosphate is an inorganic water-softening agent, functioning by precipitation of metal cations, and is the end product of hydrolysis often called reversion of pyrophosphates, tripolyphosphates, and the polymetaphosphates in aqueous solution. The reversion rate increases with temperature, is lower in alkaline solutions than in acid solutions, and metallic cations in the system (such as calcium and magnesium ions which are sequestered as complex anions) tend to decrease the stability, particularly at high pH levels (Schwartz, Perry, and Berch (1958)). Of the three condensed phosphates (pyro-, tripoly- and polymeta-), pyrophosphate hydrolyzes more slowly than tripolyphosphate, which in turn hydrolyzes more slowly than tripolyphosphate, which in turn hydrolyzes more slowly than polymetaphosphates (glassy phosphates). The reversion rates of these three classes of phosphates are each separated by an order of magnitude. For this reason pyrophosphate is often recommended rather than tripolyphosphate or the polymetaphosphates for use in chemical water softening of solutions used in cleaning reusable glass containers, despite the fact that it is not the most effective sequestering agent of the three for calcium ions and the initially soluble complex which is formed may break down, particularly at higher temperatures, and form an insoluble calcium pyrophosphate. Pyrophosphate, tripolyphosphate, and the polymetaphosphates (glassy phosphates) can sequester iron and other heavy metals in addition to calcium and magnesium (Schwartz, Perry, and Berch ((1958)). The sequestering power of all condensed phosphates is influenced by pH, temperature, and the presence of other anions in the solution.

Mehltretter, Alexander, and Rist (1953) have investigated the sequestering action of various hydroxycarboxylic acid salts toward calcium, iron, and copper. They found the calcium sequestering ability to be relatively low over the pH range 4 to 10 at 25°C. A marked increase in sequestering capacity was noted with the 6-carbon acids and tartaric acid when the solutions were made strongly alkaline (2 to 5% sodium hydroxide). In the case of gluconic and mucic acids, maximum sequestration of calcium was not obtained in caustic up to 5% concentration. On the other hand, the sequestering capacity of saccharic acid was markedly reduced in concentrations of alkali higher than 4%. The optimum sequestration with saccharic acid was found in 2 to 4% sodium hydroxide. It was pointed out that when the concentrations of saccharic and gluconic acids were increased in 3% sodium hydroxide, their sequestering power toward calcium increased in direct proportion to their concentration. Of the hydroxycarboxylic acids tested they found that potassium sodium saccharate and sodium mucate gave the best sequestration of calcium and sodium lactate the poorest. With the exception of sodium citrate, it was found that the hydroxycarboxylic acid salts failed to sequester iron or copper to any great extent at pH 7. In acid solution (pH 4) the hydroxycarboxylic acids were found relatively ineffective as sequestrants for these metals ions. However the longer chained hydroxycarboxylic acids sequestered large amounts of iron and copper in the presence of alkali compared with the shorter chained acids. The authors point out that of the hydroxycboxylic acid salts tested only gluconic is used in considerable quantity in acid and alkaline cleaning compositions. It was also noted, that in general the hydroxycarboxylic acids examined exhibited maximum sequestration in 2 to 5% sodium hydroxide solutions. They state that on the basis of their results, saccharic acid is the best general acid sequestrant in alkaline solution.

Mehltretter and Watson (1959) state that the sodium salts of gluconic, glucoheptonic, and saccharic acids are being used in increasing quantities as sequestering agents. When dissolved in caustic solutions they prevent the deposition of lime scale on bottles and bottle washing equipment. They point out that caustic solutions of these sugar acids are also of considerable importance for removing rust stains and aluminum foil labels from bottles. They state that mixtures of organic acids produced by oxidizing dextrose hydrate and corn starch with nitric acid are rich in gluconic and saccharic acids and may contain other chelating substances. The oxidation liquors from various mole ratios of these reactants were evaluated for their sequestering action toward calcium, aluminum, and ferric ions in alkaline solutions. They reported good sequestration of calcium and noted that liquors produced by oxidation of one mole of the carbohydrates with two to four moles of nitric acid gave the best results. This was attributed to a higher proportion of saccharic acid formed under these conditions. The sequestration of aluminum and of iron was also reported as quite satisfactory with alkaline solutions, but was noted to be somewhat lower than that found with sodium gluconate. They point out that such oxidation liquors have the advantage of lower cost and on this basis might be the more economical sequestrant to use.

Chaberek and Martell (1959) have discussed the use of aminopolycarboxylic acids in metal ion deactivation. They stated that these compounds form exceedingly stable alkaline earth chelates, as well as stable chelates with many transition and heavy-metal ions. They pointed out that, "these chelating agents have a number of advantages over the inorganic sequestering agents: (1) The compounds are thermally stable in aqueous solution. (2) The alkaline earth sequestering capacity remains constant over a wide pH range, in contrast to the behavior of the polyphosphates and the hydroxycarboxylic acids.(3) The stabilities of the metal chelates of the aminopolycarboxylic acids are considerably higher than those of the inorganic chelating agents, and greater reduction in the free metal ion concentration occurs. (4) The organic sequestering agents are potentially more compatible with organic systems than inorganic sequestering agents." They stated that it is evident that these compounds are at least as efficient as, and generally more efficient than, the inorganic reagents represented by the condensed phosphates. Their primary limitation at present was noted to be their relatively higher price.

An attempt is made in the following paragraphs to summarize some of the available information on the theoretical and practical behavior of the sequestering agents to be studied or of similar sequestering agents under conditions like or similar to those to be used in these investigations, in order to gather information to be used to predict or explain results:

Clements and Kennedy (1952) have presented the following comparison of the theoretical and practical sequestering power of the polyphosphates:

Table 3. Sequestering power of polyphosphates.

Sequestering agent	Total amount of polyphosphate to soften 100 ppm of calcium carbonate water	
	Theoretical, ppm	Practical, ppm
Tetrasodium pyrophosphate, $Na_4P_2O_7$	133	800
Sodium tripolyphosphate, $Na_5P_3O_{10}$	148	417
Sodium tetraphosphate, $Na_6P_4O_{13}$	154	384
Sodium hexametaphosphate, $Na_6P_6O_{18}$	204	306
Sodium heptaphosphate, $Na_9P_7O_{22}$	174	293

The theoretical quantity of sequestering agent was calculated assuming all the sodium was replaced by calcium. However it was noted that all the sodium is not so replaced and that there may be quite a big discrepancy between the theoretical and practical figures obtained, as shown above. They also observed that the sequestering power increases as the number of phosphates in the complex increases.

Chaberek and Martell (1959) have reviewed, summarized, and discussed the literature on the behavior of the polyphosphates, and the hydroxycarboxylic and aminopolycarboxylic acids. The effects of a number of factors on the sequestering properties of these agents as summarized by Chaberek and Martell are presented in the following figures: The effect of pH on alkaline earth metalion sequestration by sodium pyrophosphate, sodium tripolyphosphate and sodium hexametaphosphate is illustrated graphically in Fig. 1. They noted that increasing chain length increases the effectiveness of these polyphosphates and that the shapes of the curves were similar. In the pH range of about 7 to 9, and above 11 an increase in pH produced relatively little change in sequestration. In the intermediate pH range from about 9 to 11 the efficiency of all three phosphates

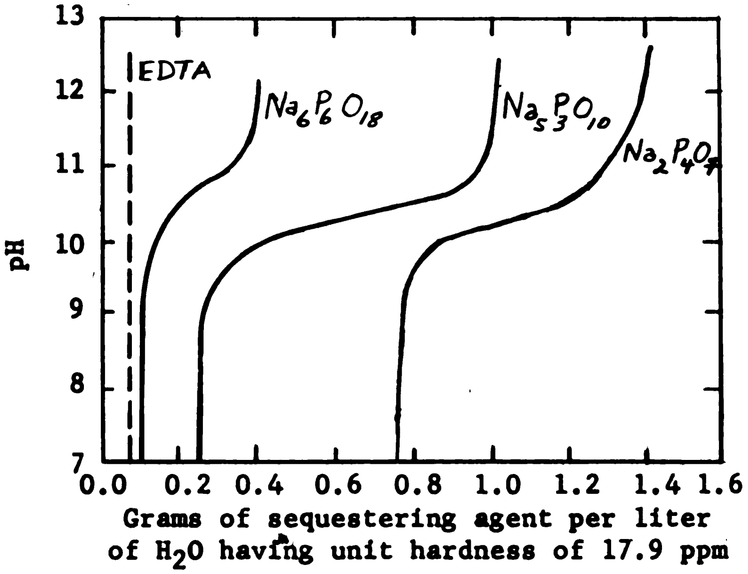

Fig. 1. Effect of pH on sequestering action of polyphosphates.

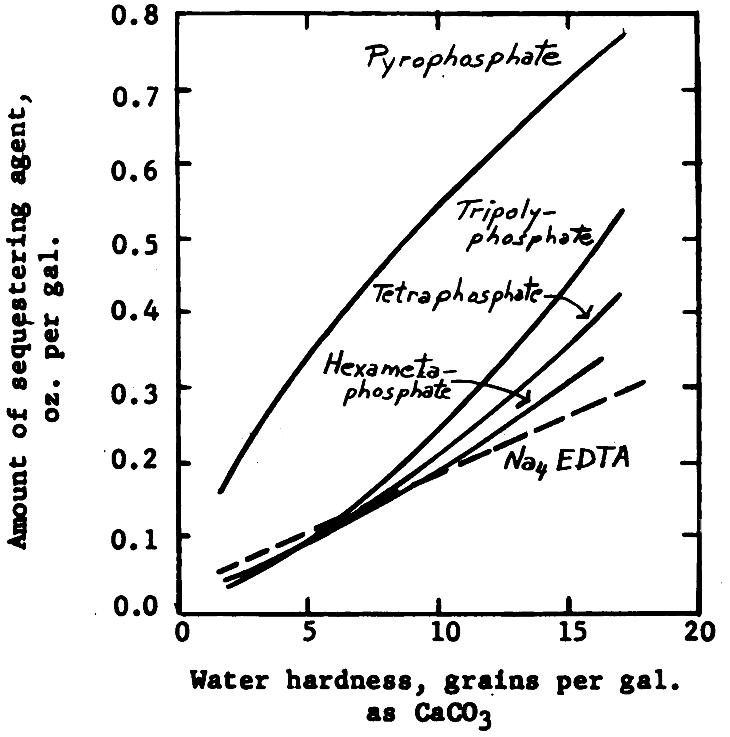

Fig. 2. Effect of water hardness on sequestering action of polyphosphates.

decreases rapidly. The relative effectiveness of the polyphosphates is also dependent on water hardness as illustrated in Figure 2. Chaberek and Martell pointed out that the amount of a particular polyphosphate required to soften water of varying hardness at 75 to 70°C is not a linear function of water hardness. An increase in water hardness from 10 to 15 grains per gallon required doubling the amount of tripolyphosphate, while an increase from 10 to 20 grain hardness required about three times the amount according to the authors. A serious disadvantage of the polyphosphates, namely their tendency to hydrolyze to the orthophosphate anion (mentioned previously) is illustrated in Figure 3 for polyphosphates of different chain lengths. This "reversion" is disadvantageous since it results in loss of sequestration ability, and in the formation of an anion having a strong tendency to precipitate metal ions. It was pointed out that reversion rates are dependent on solution pH, temperature, degree of dehydration of the polyphosphates, polyphosphate chain length; metallic cations themselves tend to increase reversion. The relative chelating capacities of citrate, gluconate, tetraphosphate, and EDTA for calcium ions has been calculated from titration data obtained with an oxalate indicator. Chaberek and Martell have reviewed, summarized and discussed these data. The results are shown in Figures 4 and 5. They noted in the pH range of 2 to 11 a low affinity of gluconic acid for the metal, which is shown by the relatively high ratio of sequestering agent to calcium required to maintain the metal in soluble form. Citric acid was considerably more efficient in the pH range 7 to 11, requiring on the average two moles of reagent per mole of metal. Tetraphosphate was described as the most effective ligand in the pH range of about 4 to 6, and between 6 and 7.5 it was comparable to EDTA which exhibited a relatively constant ligand:metal ratio of unity in the pH range 6 to 11. It was pointed out from Figure 5 by the authors that contrary to sodium gluconate's behavior in the normal pH range,it is the most effective sequestering agent in the presence of free sodium hydroxide over a wide range of concentration. It was also noted that the citrate ion is considerably better than the inorganic polyphosphate anion.

Organic sequestering agents are becoming more important and being

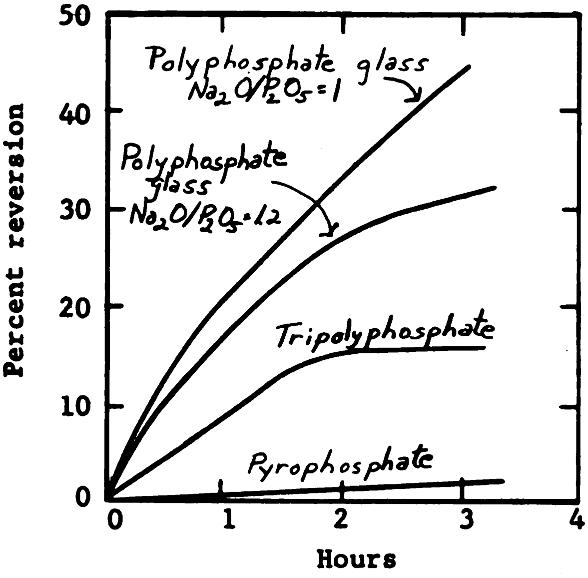

Fig. 3. Reversion rates of various polyphosphates at 100°C.

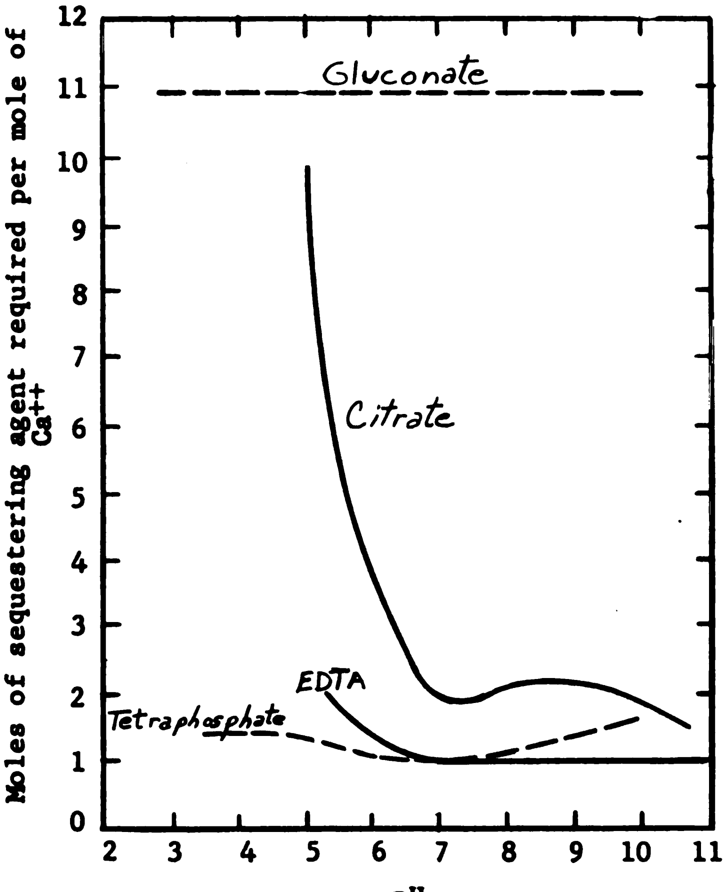

Fig. 4. Relative calcium chelating capacities of various sequestering agents as affected by pH.

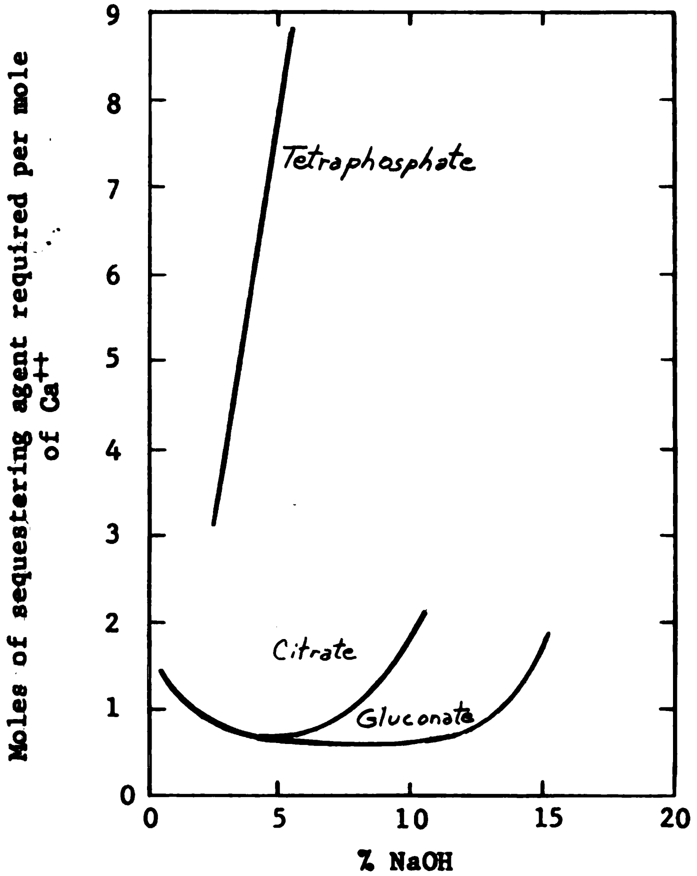

Fig. 5. Relative calcium chelating capacities of various sequestering agents as affected by sodium hydroxide concentration.

used in ever increasing quantities as water-softening agents. Such is indeed the case in the carbonated beverage industry where these agents are used in cleaning bottles. Concern has existed for some time as to what effect these agents might have on the washer itself. It is chiefly this concern, which has prompted this comparative study of the corrosiveness of these organic sequestering agents relative to that of the more commonly used inorganic phosphates and other components of the system (water, alkali, and hardness-forming salts in water).

An indication of the influence sequestering agents might have on washing equipment, in addition to their effective alkaline earth metal sequestration, is apparent from discussions of their use in metal cleaning. Chaberek and Martell (1959) have noted that alkali metal salts of aminopolycarboxylic acids such as EDTA, used with effective ferric-sequestering agents such as gluconate, citrate, and triethanolamine, should be effective in formulations for scale removal in alkaline solutions. They also pointed out that in neutral or alkaline solutions, rust may be removed by the use of an iron-sequestering agent in conjunction with a suitable reducing agent. They stated that EDTA is especially suitable for this purpose since it forms stable chelates with ferrous ion as well as with ferric and other metal ions. Aiken and Garnett (1957) have also noted that one of the outstanding properties of the EDTA group of chelating agents is their ability to "dissolve" water-insoluble metal oxides and hydroxides, carbonates, sulphates and phosphates which are formed when metals corrode. It was stated that EDTA is valuable in special-purpose cleaning compositions for metals and also as an additive to conventional alkaline cleaners. An effective industrial process using EDTA was described.

Smith (1959) has pointed out that the use of sequestering agents can be extremely valuable in obtaining a clean metal surface which is itself a primary requisite for any successful metal finishing process. He noted that both meta-silicate and polyphosphates have traditionally been used in metal cleaning processes and that EDTA can be used to advantage along with them. Further, it was noted that EDTA may be effective as a sole agent, particularly in conjunction with caustic soda. He also noted that there are hydroxycarboxylic acids which sequester iron in strongly alkaline solution and in acid conditions, and that the commercially important acid has been gluconic which is used in industrial processes in strongly alkaline media. Gluconic and tartaric acid are also used in aluminum etching solutions to prevent the formation of hard and adherent scale. Smith stated that the uses of citric, gluconic, oxalic and tartaric acids are well established for cleaning, polishing and plating of metals, and a high proportion of these uses are based on the sequestering properties of these acids and their salts.

The fact that sequestering agents are used in metal cleaning to prevent and/or remove scale would suggest that they might accelerate corrosion, since corrosion products often function as an important corrosion controlling (inhibiting) factor. The predominate cell reaction in oxygen-type corrosion of iron is

$$2Fe + O_2 + 2H_2O = 2Fe(OH)_2\downarrow$$

The ferrous hydroxide formed on the surface of the metal is insoluble and functions as the main corrosion rate controlling factor, since it limits the amount of oxidizing agent available at the cathodes for reduction (the oxygen diffusion rate is controlled by the ferrous hydroxide film). Sequestration (solubilization) of the ferrous hydroxide film could be expected to increase corrosion. This sequestration of corrosion products can be expressed by the following general reaction (used by Chaberek and Martell (1959) in their disucssions) which for purposes of simplicity and convenience does not show the valances involved, and

$$MB\downarrow + A \underset{K_x}{\overset{K_x'}{\rightleftharpoons}} MA + B$$

where B is a precipitating agent and A is a sequestering agent, which combine with the metal to give the precipitate MB and soluble chelate MA respectively. Chaberek and Martell note that the exchange constant K_x is related to K_{MA}, the metal chelate formation constant, and K_{MB}, the solubility product of MB, by the equation $K_x = \frac{1}{K_{MA}\ K_{MB}}$. It is seen that the tendency toward precipitation of the insoluble metal salt, measured by K_x is a function of both the solubility product and the metal chelate formation constant, and if K_x is sufficiently small, the precipitation of MB may be prevented. It was also pointed out that the equilibrium constant, K_x', measures the tendency of the chelating agent to solubilize slightly soluble MB and is equal to the reciprocal of K_x. Aiken and Garnett (1957) point out that this is a simplified picture of the actual situation and ignores not only the effect of conditions such as pH and concentration, but also the particle size and crystal form of the insoluble compounds. They note that it is generally easier to prevent precipitation than to dissolve a precipitate that has had time to consolidate and crystallize. Nevertheless it was noted that these relationships may sometimes be used to predict the possible usefulness of a sequestering agent on the basis of the magnitudes of the solubility product and the metal chelate formation constant.

In general, for the systems and conditions used in this investigation the relationship for predicting solubilization of MB (predominately $Fe(OH)_2$) can not be used since quantitative information on the solubility product and chelate formation constant is either not available or that which is available can not generally be adjusted to take into account the deviations the systems and conditions impose. This problem has been expressed another way in a bulletin entitled "Keys to Chelation" (1959) in which it was stated that, "most industrial chemical systems which benefit by the addition of metal-control agents are not simple systems of water and the metal ions. If they were, the selection of the proper agent and the most efficient use concentration would be a clear-cut decision based on the stability constants. It would then be possible to state definitely that so much of an agent would do a particular job. Unfortunately, complicating factors due to other materials in the system profoundly affect the metal-chelation reaction." The following environmental factors were noted to disturb the simple metal-chelate equilibrium: (1) Temperature, (2) Other metal ions, (3) Other anions, (4) Ionic strength effect, and (5) pH. It was pointed out that of all these factors, and aside from the stability constant, the most important factor to be considered is the pH of the system.

Since it seems reasonable to expect that water softening agents would affect the nature and distribution of corrosion products this investigation is conducted to determine if such is the case and to what relative extent agents (sequestering agents) either accelerate or inhibit corrosion of mild steel, in systems commonly employed in the cleaning of reusable glass containers.

EXPERIMENTAL DESIGN AND ANALYSIS

The purpose of this investigation is to assess the corrosion inhibiting or accelerating effects of organic sequestering agents, relative to the effects of the more traditionally used inorganic phosphates and other components of the system under conditions similar to and varied in accordance with those commonly encountered in practice.

The general experimental design to be employed in this investigation is shown in Figure 6. The treatments consist of different agents, agent combinations and agent concentrations. The blocks or outcome groups consist of five consecutive seven-day immersions. Each cell or experimental unit consists of four observations (or replications).

A symbolic representation of such a two-way table with t treatments, b blocks, and equal numbers of observations in each cell is presented in Table 4. Table 5 gives a symbolic description of analysis of variance of a two-way table with t treatments, b blocks and equal numbers of observations in each cell. The notation employed is rather general in statistics. A dot in a subscript indicates summation. The k th observation made in the j th block on the i th treatment (i = 1...t, j = 1...b, and k = 1...n (n = 4)) is denoted by X_{ijk}. Additional convenient notation employed here follows: $X_{ij.}$ = the sum of the observations in the cell which is located in the i th treatment and the j th block. $X_{i..}$ is the sum of all observations in the i th treatment and $X_{.j.}$ the sum in the j th block. X is the sum of all the observations.

For the proper evaluation of experimental data the analysis of variance model employed must be specifically stated. Steel and Torrie (1960) and Snedecor (1956) discuss the various models in considerable detail. Discussions appropriate to this investigation are presented by Steel and Torrie in their chapter on analysis of variance of multi-way classifications (Section 8.8 Linear models and the analysis of variance.) and by Snedecor in his chapter on factorial arrangements of treatments (Section 12.5 The two-factor experiment.). Both references present component analyses (variance components) and procedures for test-

Fig. 6. Experimental design. Agent codes: (0) Distilled water; (1) 3% Sodium hydroxide; (2C1) 3% Sodium hydroxide +0.042% sodium gluconate; (2C2) 3% Sodium hydroxide + 0.084% sodium gluconate; (2C4) 3% Sodium hydroxide +0.168% sodium gluconate; (3C1) 3% Sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate; (3C2) 3% Sodium hydroxide +0.156% tetrasodium ethylenediaminetetraacetate; (3C4) 3% Sodium hydroxide +0.312% tetrasodium ethylenediaminetetraacetate; (4) 3% Sodium hydroxide +0.057% trisodium phosphate (($Na_3PO_4 \cdot 12H_2O$)); (5) 3% Sodium hydroxide +0.293% tetrasodium pyrophosphate (($Na_4P_2O_7 \cdot 10H_2O$)).

Blocks (immersions)	Treatments (agents)									
	0	1	2C1	2C2	2C4	3C1	3C2	3C4	4	5
1	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —
2	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —
3	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —
4	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —
5	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —	— — — —

Table 4. Symbolic representation of a two-way table with t treatments, b blocks, and equal numbers of observation (n = 4) in each cell, k = 1...n.

Treatments i = 1...t	Blocks, j = 1...b					Treatment sums	Treatment means
	1	. . .	j	. . .	b		
1	X_{111}		X_{1j1}		X_{1b1}		
	X_{112}		X_{1j2}		X_{1b2}		
	X_{113}		X_{1j3}		X_{1b3}		
	X_{114}		X_{1j4}		X_{1b4}		
Sums	X_{11}		X_{1j}		X_{1b}	$X_{1.}$	
Means	$\bar{X}_{11}$		$\bar{X}_{1j}$		$\bar{X}_{1b}$		$\bar{X}_{1.}$
.							
.							
.							
i	X_{i11}		X_{ij1}		X_{ib1}		
	X_{i12}		X_{ij2}		X_{ib2}		
	X_{i13}		X_{ij3}		X_{ib3}		
	X_{i14}		X_{ij4}		X_{ib4}		
Sums	X_{i1}		X_{ij}		X_{ib}	$X_{i.}$	
Means	$\bar{X}_{i1}$		$\bar{X}_{ij}$		$\bar{X}_{ib}$		$\bar{X}_{i.}$
.							
.							
.							
t	X_{t11}		X_{tj1}		X_{tb1}		
	X_{t12}		X_{tj2}		X_{tb2}		
	X_{t13}		X_{tj3}		X_{tb3}		
	X_{t14}		X_{tj4}		X_{tb4}		
Sums	X_{t1}		X_{tj}		X_{tb}	$X_{t.}$	
Means	$\bar{X}_{t1}$		$\bar{X}_{tj}$		$\bar{X}_{tb}$		$\bar{X}_{t.}$
Block sums	$X_{.1}$		$X_{.j}$		$X_{.b}$	X	
Block means	$\bar{X}_{.1}$		$\bar{X}_{.j}$		$\bar{X}_{.b}$		$\bar{X}$

ing main effects and interaction effects for the various models. Steel and Torrie's presentation is more recent and easier to follow. Common models of analysis of variance (Steel and Torrie (1960) and Snedecor (1956)) are the fixed effects model or Model I, the random effects model or Model II, and the Mixed model. The Mixed model calls for at least one criterion of classification to involve fixed effects and another to involve random effects.

Steel and Torrie (1960) state that, "in randomized complete-block

Table 5. Symbolic description of analysis of variance of a two-way table with t treatments, b blocks, and equal numbers of observations in each cell.

Source of variation	Degrees of freedom	Sum of squares	Computational formula for sum of squares
Total	ntb-1	$\sum_i\sum_j\sum_k(X_{ijk}-\bar{X})^2$	$\sum_i\sum_j\sum_k X_{ijk}^2-\frac{X^2}{ntb}$
Treatments	t-1	$nb\sum_i(\bar{X}_{i.}-\bar{X})^2$	$\frac{1}{nb}\sum_i X_{i.}^2-\frac{X^2}{ntb}$
Blocks	b-1	$nt\sum_j(\bar{X}_{.j}-\bar{X})^2$	$\frac{1}{nt}\sum_j X_{.j}^2-\frac{X^2}{ntb}$
Interaction	(t-1)(b-1)	$n\sum_i\sum_j(\bar{X}_{ij}-\bar{X}_{i.}-\bar{X}_{.j}+\bar{X})^2$	$\frac{1}{n}\sum_i\sum_j X_{ij}^2-\frac{1}{nb}\sum_i X_{i.}^2-\frac{1}{nt}\sum_j X_{.j}^2+\frac{X^2}{ntb}$
Error	tb(n-1)	$\sum_i\sum_j\sum_k(X_{ijk}-\bar{X}_{ij})^2$	$\sum_i\sum_j\sum_k X_{ijk}-\frac{1}{n}\sum_i\sum_j X_{ij}^2$

design problems where the fixed effects model is appropriate, two or more treatments are selected for testing. These are not randomly drawn from a population of possible treatments but are selected, perhaps as those which show the most promise or those most readily available. All treatments about which inferences are to be drawn are included in the experiment. Block effects are also fixed and inferences about treatments or blocks are not intended to apply to blocks not included in the experiment." Steel and Torrie point out that the distinction between the models is that for the fixed model, a repetition of the experiment would bring the same set of treatments (or components for the populations involved) into the new experiment and our attention is concentrated on these treatments. For the random model, a repetition would bring in a new set of treatments but from the same population and we would be interested in variability of the treatments since we are not in a position to continue our interest in a specific set. With the fixed model we draw an inference about the population of treatments.

Steel and Torrie (1960) discuss the testing of main effects for these models. They point out that when the sources of variation are assumed to be random, the experimental error (residual error) is the appropriate error for testing hypotheses concerning main effects. They go on to point out that in the case where main effects are assumed to be fixed, one does not necessarily assume that the experimental error is random. Further, when nonrandomness is assumed, essentially there are fixed effects for each block-treatment combination (where blocks and treatments are the main effects) over and above the treatment and block contributions. This can be stated another way by saying that the differences in responses to the various treatments are not of the same order of magnitude from block to block and this cannot be called a random effect. Steel and Torrie point out that when the contribution referred to as experimental error is not random, they relabel it as interaction and that the sampling error is an appropriate error for testing hypotheses concerning interaction and hypotheses concerning main effects.

Steel and Torrie present a table of average values of mean squares for a randomized complete-block analysis to show what sort of conclusions can be drawn from tests of significance, in the form of ratios of mean squares. Included in this table are the linear models for the fixed effects model with and without interaction, and with and without sampling (X_{ij}, an observation from the j th block on the i th treatment, i = 1,..., t treatments and j = 1..., r blocks; X_{ijk}, the k th observation made in the j th block on the i th treatment, i = 1,..., t, j = 1,..., r, and k = 1,..., s observations; μ, the population mean; τ_i, a treatment contribution; β_j, a block contribution; $(\tau\beta)_{ij}$, an interaction contribution; ϵ_{ij}, an experimental contribution; δ_{ijk}, a sample contribution). The portion dealing with the fixed effects model or Model I follows in Table 6.

Steel and Torrie state that, "for the fixed model with no interaction, both block and treatment effects can be tested by residual or error mean square. Even when we have only one sample, S = 1, per experimental unit, valid tests are possible. In this case, it is not possible to estimate σ^2. However, when there are fixed interaction effects, it is not possible to make any valid F test when there is no sampling. When s observations are made in each cell s>1, sampling error is a valid error for testing interaction, treatment, and block mean squares."

For the experimental design employed in this investigation the

Table 6. Average values of mean squares for a randomized complete-block analysis (from Steel and Torrie (1960); Table 8.6).

Source	Degrees of freedom	Fixed model, no interaction	
		No sampling	Sampling
		$X_{ij} = \mu + \tau_i + \beta_j + \epsilon_{ij}$	$X_{ijk} = \mu + \tau_i + \beta_j + \epsilon_{ij} + \delta_{ijk}$
Blocks	r-1	$\sigma_\epsilon^2 + t\sum \beta_j^2/(r-1)$	$\sigma^2 + s\sigma_{\tau\beta}^2 + st\sum \beta_j^2/(r-1)$
Treatments	t-1	$\sigma_\epsilon^2 + r\sum \tau_i^2/(t-1)$	$\sigma^2 + s\sigma_{\tau\beta}^2 + sr\sum \tau_i^2/(t-1)$
Residual	(r-1)(t-1)	σ_ϵ^2	$\sigma^2 + s\,\sigma_{\tau\beta}^2$
Sampling error	rt (s-1)		σ^2

Source	Degrees of freedom	Fixed model, interaction	
		No sampling	Sampling
		$X_{ij} = \mu + \tau_i + \beta_j + (\tau\beta)_{ij} + \epsilon_{ij}$	$X_{ijk} = \mu + \tau_i + \beta_j + (\tau\beta)_{ij} + \delta_{ijk}$
Blocks	r-1	$\sigma_\epsilon^2 + t\sum \beta_j^2 /(r-1)$	$\sigma^2 + st\sum \beta_j^2/(r-1)$
Treatments	t-1	$\sigma_\epsilon^2 + r\sum \tau_i^2/(t-1)$	$\sigma^2 + sr\sum \tau_i^2/(t-1)$
Residual	(r-1)(t-1)	$\sigma_\epsilon^2 + \sum_{i.j} (\tau\beta)_{ij}^2 /(r-1)(t-1)$	$\sigma^2 + s\sum_{ij} (\tau\beta)_{ij}^2 /(r-1)(t-1)$
Sampling error	rt (s-1)		σ^2

fixed effects model(Model I) seems most appropriate for the analyses. The treatments and blocks were not randomly drawn from a population of possible treatments or from a population of possible blocks, but were selected for testing. Treatments and blocks about which inferences are to be drawn are included in the experiment. Block and treatment effects are therefore considered to be fixed.

The experiments conducted in this investigation are of the two-way classification (or two-factor) type, with agents as the treatments and immersions as the blocks. The linear equation representing a single observation (or replicate corrosion weight loss) is, $X_{ijk} = \mu + \tau_i + \beta_j + (\tau\beta)_{ij} + \delta_{ijk}$. The i th agent over-all mean can be represented by $\bar{X}_{i.} = \mu + \tau_i + \bar{\beta}_. + \overline{(\tau\beta)}_{i.} + \bar{\delta}_{i.}$ and the j th immersion over-all mean can be represented by the $\bar{X}_{.j} = \mu + \bar{\tau}_. + \beta_j + \overline{(\tau\beta)}_{.j} + \bar{\delta}_{.j}$. These equations show the components of an agent or immersion over-all mean and what is involved in agent and immersion over-all mean comparisons. When factor (agent or immersion) over-all means are tested for significance and the model is conformed to, the components of the over-all mean that are deviation means, contribute essentially a zero effect to the difference between the factor (agent or immersion) over-all means being compared.

DEVELOPMENT OF EXPERIMENTAL PROCEDURE

INTRODUCTION

Corrosion consists of reactions between a metal and its environment, thus, corrosion behavior is a property both of the metal and environment to which it is exposed. Factors associated with both phases must be considered and controlled to establish satisfactory exposure conditions during a corrosion test. There is, therefore, no universal standard test procedure.

Literature pertaining to the development of a satisfactory procedure for the evaluation of corrosion of mild steel in alkaline sequestering agent solutions follows.

REVIEW OF LITERATURE

There are certain characteristics of this investigation that may yield to an established general method of corrosion testing. The following literature provides a review of the generally accepted corrosion testing methods and is presented to provide a basis for the methods employed.

Jelinek (1959) and Borgmann (1948) summarize the major methods for measuring the amount and intensity of corrosion as well as certain qualitative aids in determining the amount of corrosion. They both point out that the use of two or more methods will remove many of the criticisms given for the individual methods. A brief description of the individual methods outlining the fields of usefulness and the major advantages and limitations follows.

Visual observation may be useful to detect occurrence of attack and identify its general nature; it is a simple method and is often valuable in conjunction with other methods; however it is subject to human error and is qualitative.

Loss in weight is useful to determine the extent and rate of uniform corrosion; it is simple, quantitative and direct. However, the method is subject to error due to incomplete removal of corrosion products and loss of uncorroded metal, special types of attack are not measured, and multiple specimens are necessary.

Gain in weight is useful to determine the extent and rate of uniform corrosion where no loss of corrosion products occurs. It is particularly applicable to indoor atmospheric corrosion and high temperature oxidation studies, and error due to improper removal of corrosion products is eliminated. However, an analysis of corrosion products must be made in order to determine loss of metal, moisture in corrosion products may vary in amount and thus influence the results, and special types of attack are not measured and accidental loss of corrosion products would introduce an error.

Electrical resistance change can be used in gaseous or poorly conducting environments or in other environments if the specimen is removed for measurement. In addition to its usefulness in evaluating environment corrosivity it can be used to follow certain property and composition changes, and the method is non-destructive and adaptable to continuous measurement. However, the method is indirect, requires calibration, does not distinguish between types of attack, is subject to surface-to-volume errors, and if small wires are employed, the attack may be different in amount from that on a more massive specimen.

Hydrogen evolution may be followed for tests in which corrosion takes place solely with hydrogen evolution. The method is adaptable to rate measurement, but does not determine the distribution of attack.

Oxygen absorption is useful in tests where corrosion takes place mainly with the absorption of oxygen. The method is adaptable to rate measurement, but does not determine the distribution of attack, and an analysis of corrosion products is required for metals capable of existing in more than one ionic state.

Depth of pitting measurements (other than microscopic) are useful for tests made to determine the serviceability of metals as containers of fluids. The method is especially adapted for use with methods of determining total attack, and it gives a correct measure of penetration of a metal by corrosion except when the attack is intergranular. However, many specimens are required to determine time-penetration curves, and difficulty occurs in obtaining accurate measurement.

Microscopic methods are useful to determine the kind of attack, to measure the depth of pits, and to determine the constituents of the metal that are specially capable of initiating attack. It is an excellent tool to supplement other measures, but is not generally useful in making quantitative measurements.

Physical property changes of material can be used to evaluate their deterioration; methods that can be used for this purpose are tensile strength, ductility, impact, resistance, and hardness. This method allows a direct measure of the changes in physical properties and hence is of practical value to the structural engineer; however, a resultant of the several possible attacks is measured and it is not possible to evaluate the damage resulting from each type of attack separately.

The electrochemical methods that may be useful are: measurements of single electrode potential, potential difference between unlike metals, shorted-cell current, anode and cathode polarization, and film resistance.

Single electrode potential methods are useful to study film formation and breakdown at a metal surface. The method distinguishes between anodic and cathodic control, and measures the electrochemical driving force. It does not measure extent or rate of attack and careful interpretation of results is required.

The measurement of the potential difference between dissimilar metals is a useful method to study galvanic effects; it measures the relative tendency to corrode, but is qualitative only.

Shorted-cell current measurement is useful to measure the extent of corrosion relative to a standard noble metal. The measurement is simple, but an arbitrary choice of a cathode metal may distort the normal influence of such areas on the metal under study. The anode and cathode are separated by a much greater distance than usual, hence resistance of solution and the unnatural formation of corrosion products are sources of error.

Anode and cathode polarization methods are useful to study galvanic and concentration cell corrosion and to determine the total polarization current. The method yields a semi-quantitative estimate of the corrosion rate, but does not measure the distribution of attack.

Film resistance measurements may be used to determine the penetrability of surface films by various anions. A qualitative measure of the influence of the anion on the probability of breakdown of the film is obtained. However, an arbitrary standard voltage is usually employed, and care must be taken that other reactions do not interfere. One may measure the decomposition voltage of an electrolyte-metal system without reference to a surface film.

The electrometric method is useful to measure the thickness of surface films. The technique is simple and quite exact, but only useful on adherent, thin, surface films of some metals.

Optical methods are useful to study the growth of tarnish and other surface films. Formation and growth of films can be studied without disturbance of the system. Relatively complicated apparatus is required. Results of simpler relectivity methods are difficult to interpret quantitatively.

Environmental analysis is useful to study product contamination from corrosion and to follow relative corrosion of metal components. The analysis may be necessary for product specifications. The method is often applicable to measurement of trace quantities and is useful in liquid metal corrosion studies. It does not show the distribution of attack on the metal and a material balance is required to evaluate liquid metal corrosion.

It was decided from the above information that the weight loss and visual observation methods would be used for this investigation. The weight loss method facilitates a simple, direct, quantitative measure of the extent and rate of corrosion. The visual observation method which is simple and of value in conjunction with other methods is useful to detect the occurrence of attack and identify its general nature. The principal limitations of the two methods are that multiple specimens are required and that caution need be exercised in the selection or development of a treatment to remove corrosion products.

Evans (1960) points out that in wet corrosion, the measure of the progress of attack is often the loss of weight after exposure. Fontana (1960) states that, "change in weight of the specimens is most often used as a measure of corrosion or the basis for calculation of the corrosion rate." Champion (1952) also points out that the gravimetric method is normally used for determining the metal remaining after corrosion.

Corrosion being a complex phenomenon, influenced primarily by factors pertaining to the metal and the environment, makes it generally impossible to have any one detailed corrosion test procedure that will fit a number of different corrosion problems. Once the particular method has been chosen, it is best to acquire a general understanding of the basic principles underlying the detailed procedures commonly employed in the particular method. With this understanding the investigator is then in a position to develop, with the aid of the available literature, a detailed experimental procedure best suited to the particular problem. In some cases the recommendations available in the literature pertaining to a particular detailed procedure are adequate, in others modifications are required, and in still others new detailed procedures have to be developed in order to obtain the best over-all experimental procedure. It is the purpose of the literature to follow, and the results pertaining to the development of the experimental procedure presented later, to provide a background and basis for the utilization of particular detailed procedures to be followed in this study. The value and reliability of the data obtained are dependent upon the details involved.

Champion (1952), Borgmann (1948), and Speller (1935) present a comprehensive discussion of general corrosion testing procedures based on the literature in this field. They discuss the general procedures to be followed in total immersion corrosion tests. The American Society for Testing Materials (ASTM) presents specific detailed test procedures for use to evaluate a number of corrosion problems. A review of factors pertaining to the metal, corrosion media, exposure conditions, and assessment of effects on the metal and media important in the development of the experimental procedure follows:

Factors pertaining to the metal are selection of the specimens, size, and shape of specimens, replication and number of immersion periods, preparation of specimens, and cleaning of the specimens after corrosion. Champion (1952) points out that test specimens should be representative of the material under test. He states further, "that rolled products are most widely used because they provide the following advantages: (1) They are most extensively used in service. (2) A wide range of thicknesses can be obtained. (3) Major variations in corrosion resistance over the surface of a rolled sheet are unusual. (4) Sheets of large surface area can be obtained thus permitting the preparation of a large number of replicate specimens and also analytical samples from the same sheet. (5) Relatively simple methods of preparation of the specimens from the sheet can be employed."

The ASTM (1952) in discussing test specimens and their preparation states that, "the size and shape of specimens will vary with the purpose of the test, the nature of the materials to be tested, and the testing apparatus to be used. The size may also be limited by the necessity of preserving a proper ratio between the area of the specimen and the volume of the testing solution when the latter must be limited. In general, an effort should be made to have the ratio of surface to mass large and that of edge area to total area small. The shape and dimensions of the specimens shall be such as to permit weighing on an accurate balance and to facilitate accurate measurement and calculation of the area of each specimen. Such measurements of dimensions shall be made accurately to the nearest 1/64 in. (0.5 mm) for length, width or diameter; and to the nearest 0.001 in. for thickness."

Champion (1952) and Knapp (1948) point out that the size and area adopted is often determined by experimental convenience, but that it is desirable to adopt a standard size as far as possible to insure that comparable results will be obtained. They suggest the use of simple shapes as being most desirable. In addition, it is advantageous to adopt a size and shape of specimen giving a low edge to surface area ratio and a reasonably large area. Champion (1952) states that, "a thickness of 0.036 in. is convenient for many purposes and that the French Aeronautical Committee have adopted 0.039 in. (1 mm) for sheet thickness." He also states that, "the German specification on corrosion tests in general recommends that the dimensions should be not less than 5 x 2 cm."

Fontana (1960) points out that the specimen should be carefully measured to permit calculation of the surface area, since area enters in the formula for calculating the corrosion rate. He states that, "the original area is used to calculate the corrosion rate throughout the test. If the dimensions of the specimen change appreciably during the test, the error introduced is not important because the material is probably corroding at too fast a rate for its practical use in the intended application."

Borgmann (1948) points out that even when the greatest pains are taken in the corrosion test it is not to be expected that absolute reproducibility will be achieved, since there are factors beyond the control of the experimenter. However, statistical control is often achieved. The absolute error of measurement can be reduced only be increasing the number of specimens tested. The type of attack that occurs can greatly influence the reproducibility of the results. The reproducibility will in general be much greater if the attack is uniform than if the attack occurs at a few discrete points.

Evans (1960) points out that in general, it is well to perform all experiments in duplicate or triplicate. He notes that in the case of localized corrosion this will not be enough replicates for good reproducibility.

The ASTM (1958) standard method of total immersion corrosion test for soak tank metal cleansers recommends that at least two, and preferably four, replicates shall be tested in each cleaner solution.

Champion (1952) states that, "a minimum of three replicates has been recommended as a general rule." He also points out that when it is known that the corrosion rate is constant from the beginning of exposure, a single replicate set of specimens will suffice. With non-linear corrosion time curves further replicates are necessary, and where the shape of the corrosion time curve is not known, it is recommended that at least three replicate sets should be exposed for withdrawal after increasing periods of time. However, the degree of replication to be adopted will depend on the accuracy required in the mean result and the scatter which is to be expected in the individual results.

An ASTM (1952) method, which describes procedures for making total immersion corrosions tests, discusses the problem of determining the number of specimens to be used from a statistical approach. They state that, "observations on some typical metals immersed under controlled conditions in typical corrosive media have indicated that the coefficient of variation may reasonably be expected to be less than 7 percent." With such a coefficient of variation, the expected limits of error of the average of groups of various sizes can be estimated for a desired statistical probability. They refer to the work of Humes, Passano, and

Hayes (1930) when presenting their statistical procedures. They state that, "E, error of average in percent = $\frac{ZV'}{\sqrt{N'}}$ where: Z = 1.96 for a statistical probability, P, of 0.95; V' = universe coefficient of variation of 7 percent; and N = number of repititions or specimens. Therefore, the expected errors of the average of different numbers of the specimens would be N = 8, E = ± 4.8 percent; N = 4, E = ± 6.9 percent; and N = 2, E = ± 9.7 percent." It was stated that, "running total immersion tests in quadruplicate would make it highly probable that the average would be within 7 percent of the true average. This should be satisfactory for most corrosion research programs."

Care must be taken to properly clean and prepare specimens for tests. The surface preparation will vary with the type of test. Surface preparation usually consists of a pre-cleaning or degreasing operation to remove surface contamination. A pickling process (pickling is the term applied to the chemical removal of surface oxides from metal by immersion in an acid solution) may be required to remove scale and provide a more uniform, reproducible surface condition.

Fontana (1960) states that ideally the surface of the test specimen should be identical with the surface of the actual equipment to be used in the plant. However, this is usually an impossible condition, because the surface of commercial metal and alloys vary as produced and as fabricated. The degree of scaling or amounts of oxide on the equipment varies and also the condition of other surface contaminants. Because of this situation and because the determination of the corrosion resistance of the metal or alloy itself is of primary importance in most cases, a clean metal surface is usually used. A standard surface condition is also desirable and necessary in order to facilitate comparison with results of others.

Champion (1952) points out that extremely thin, invisible films of grease can interfere with the corrosion process. Evans (1960), Jelinek (1959), ASTM (1952), Knapp (1948), and Meyer (1948) also note the importance of removal of grease and other surface contaminants.

Champion (1952) and Meyer (1948) discuss in considerable detail the general methods for metal precleaning and degreasing. The solvent and vapor cleaning methods are: simple solvent cleaning, emulsifiable solvent cleaning, and vapor degreasing.

The ASTM (1958) and Champion (1952) describe in detail various apparatus, cleaning solutions, and laboratory procedures for degreasing of corrosion test specimens.

Evans (1960), Champion (1952), ASTM (1952)and McCollam and Warrick (1948) suggest that pickling of the specimens may be required to remove surface scale and provide a uniform, reproducible surface. Wesley (1943) found it necessary to remove 0.0003 in. thickness from the surface of some commercial alloy specimens to obtain adequately reproducible results. Hoar (1948) obtained reproducible results from the corrosion of steel in acid when the specimens were pickled.

McCollan and Warrick (1948) point out that wide variations are possible in the type, strength and temperature of the acid solutions used in pickling. In addition, pickling inhibitors may be added to acid pickling solutions. They are agents which diminish the attack of the acid on the metal areas from which the scale has been removed, without appreciably retarding the rate at which the acid removes scale or rust. The procedure used depends on the material to be pickled, the character of the scale involved and the surface desired after pickling.

Evans (1960), Jelinek (1959), Champion (1952), ASTM (1952), Knapp (1948) and Speller (1935) all point out that in tests where the corrosion is assessed by weight loss, it is necessary to remove the corrosion products from the specimen after exposure. It is essential that the specimens be thoroughly cleaned of all corrosion products without loss of any base metal. The literature points out that there are many satisfactory methods of cleaning specimens but, whatever the method, its effect in removing base metal should be determined for each material. The appraisal of the amount of attack should determine the cleaning method. Drastic methods should not be used when there are indications of only a small weight loss resulting from the corrosion test.

Champion (1952) and Knapp (1948) discuss in detail the general methods for corrosion products removal from metal specimens. The various methods of corrosion products removal may be classified as: Mechanical treatment by such means as wet scrubbing with a bristle brush, abrasive and detergent (a satisfactory method for removing light non-adherent films). Chemical treatments using various chemical reagents are often employed, but are generally specific for certain materials. Electrochemical treatment, with the specimen as cathode, has been found useful with a large number of metals and alloys, but the possibility exists that deposition of metal from dissolved corrosion products or contaminants in the solution may occur.

Champion (1952) and Knapp (1948) present specific procedures taken from or based on available literature for corrosion products removal from iron and steel. Champion describes the use of such solutions as sulphuric acid, Clarke's solution (composed of hydrochloric acid, antimonious oxide, and stannous chloride), ammonium citrate solution, and sodium hydroxide solution for simple chemical treatment of iron and steel corrosion products.

The ASTM (1958) and Speller (1935) suggest immersion of the specimens for 2 to 3 minutes in a boiling solution of ammonium citrate (10 percent by weight) for removal of corrosion products from iron and steel.

Evans (1960), ASTM (1958) and Speller (1935) suggest the use of a warm dilute acid solution containing sufficient inhibitor to prevent attack of the base metal.

Evans (1960) states that, "for the removal of the corrosion-product, inhibited acid is generally recommended; preliminary experiments are necessary to find the lowest concentration which will remove all the products without seriously attacking the metal."

The corrosion media or environment is another important factor in corrosion. Champion (1952) presents a general discussion of corrosion media, based on the literature. He points out that the choice of corrosion media depends upon the test objectives and that in fundamental research it is often important to avoid complications as far as possible, so that a simple pure solution or liquid may be required. With the aid of the literature he lists the following characteristics of the environment which should be considered and points out that their relative importance varies with different systems: (1) Composition. (2) Concentration. (3) Concentration gradients. (4) Particle size of any solids constituting the whole or part of the environment. (It was pointed out that the intensity of corrosion tends to increase to a maximum with increasing particle size, while the area of attack is more likely to decrease.) (5) Humidity of gases and vapor. (6) Frequency of renewal or replenishment of the corrosive.

The ASTM (1952) also points out that test solutions should be made up accurately, with the composition controlled to the fullest extent possible and that the composition of the test solution should be determined by chemical analysis.

A review of factors pertaining to exposure conditions follows:

Wesley (1948) states that, "perhaps the most common danger of mistaken interpretation of laboratory immersion test results arises from exhaustion of ingredients in the original solution which control the rate or type of corrosion, or from accumulation of products which are corrosion inhibitors or accelerators." This emphasizes the importance of volume of solution per area of specimen and adequate replenishment of solutions. Listed in Table 7 are some of the recommended ratios for volume of solution per square centimeter of metal surface.

Table 7. Recommended ratios of solution volume to metal surface area.

Source	Volume per square centimeter	Surface area per 500 milliliter
"Corrosion" (1956)	50.0 ml	10.0 cm^2
Wesley (1948)	40.0 ml	12.5 cm^2
Champion (1952)	33.3 ml	15.0 cm^2
Calcott, Whetzel, and Whittaker (1923)	8.3 ml	60.0 cm^2
ASTM (1958)	6.7 ml	75.0 cm^2

Champion (1952) also pointed out that the volume of solution recommended per square centimeter of metal surface has varied from 6 ml to 40 ml. The important point is that the volume of the testing solution should be large enough to avoid any appreciable change in its corrosiveness either through the exhaustion of corrosive constituents, or the accumulation of corrosion products that might affect further corrosion.

Wesley (1948) and ASTM (1952) point out that each specimen should be tested in a separate container, since it has been found that the practice of testing several specimens of the same material in a single container gives results which do not measure the true variability of the test as determined by repeated separate tests. In addition, containers and specimen supports should be used which do not affect the corrosion process.

Temperature control of the corrosion media is another important exposure condition to be considered. Champion (1952) suggests that temperature control to ± 0.5^{o}C (± 0.9^{o}F) is often regarded as adequate for many corrosion tests. Wesley (1948) and ASTM (1952) point out that thermostatic control at the desired temperature, ± 1^{o}C (± 1.8^{o}F) is usually considered satisfactory.

An important consideration in any corrosion test is its duration and the number and length of exposure periods (or immersion periods) to be employed.

Speller (1935) presents the following discussion of corrosion test duration. He points out that in general the initial rate of corrosion is much greater than after the action has proceeded for some time. He states that, "one good example of this is found in alkaline solutions where the initial rate may be several times greater than the rate after a few hours." Calcott and Whetzel (1923) state that in many cases of chemical corrosion the rate becomes essentially constant after 48 hours. Speller mentions further that in any case, the retardation that follows the initial rate of corrosion is dependent to a large extent upon the character of the corrosion product deposited on the metallic surface, and that this should be determined for a specific case and allowed for, as otherwise the results of short-time tests may be very misleading. Speller summarizes by pointing out that in all cases the length of test should be determined by the length of time required to produce a reasonable amount of corrosion.

Wesley (1948) states that, "a constant rate of corrosion is encountered much more often in total immersion than in other types of corrosion." In addition, he points out that if the test is too short, some materials which build up protective corrosion product films slowly may be ruled out as unsatisfactory and if the test is too long, the effects of exhaustion of ingredients or accumulation of corrosion products may be pronounced.

The ASTM (1952) points out that the duration of the corrosion test will be determined by its nature and purpose. They mention further that in some cases it will be desirable to expose a number of specimens so that certain of them can be removed after definite time intervals so as to provide a measure of change of corrosion rates with time. In addition, they indicate that any procedure that requires removal of solid corrosion products between periods of exposure of the same specimens will not measure accurately normal changes of corrosion with time since the effect of corrosion products on subsequent corrosion is not evaluated. They suggest also that the higher the rate of corrosion, the shorter may be the testing period.

Fontana (1960) also points out that proper selection of exposure time and number of exposure periods are important, and misleading results may be obtained if they are not considered. He states that in most cases at least two periods should be used, since this procedure provides information on changes in corrosion rate time and may uncover weighing errors (if a test consists only of an original and a final weighing, an error in either case might go undetected and be reflected directly in the results.) He points out that the corrosion rate may increase, decrease, or remain constant with time, but quite often the initial rate of attack is high and then decreases. He notes further that a widely used procedure in the laboratory is to use five 48-hour periods with fresh solution for each period. He suggests that the test time should be reported particularly if exposure time is short.

The next important phase is assessment of the corrosion. Champion (1952) has reviewed and discussed the assessment of corrosion effects on metal and media. He includes considerable information on quantitative and qualitative assessment by gravimetric and macroscopic methods, respectively. Champion notes that the frequency of inspection or examinations depends on the metal, its environment, the object of the test, and the method of assessment. He points out that the analytical balances available in most laboratories provide adequate accuracy for many corrosion tests, and that this general availability of suitable apparatus is no doubt largely responsible for the extensive use of gravimetric methods for the quantitative assessment of corrosion. He mentions that determinations of loss of weight can be used over a much wider range of conditions than gain in weight, although the accuracy may be lower when cleaning of the specimen after exposure is necessary. The ASTM (1952) states that after the corroded specimens have been cleaned, they should be reweighed with the same accuracy as the original weighing of ± 0.0005 g.

Fontana (1960) points out that in many cases, visual observation of the specimens on removal from the test solution provides valuable information concerning the causes or mechanism of the corrosion involved.

Champion (1952) points out that in macroscopic examination it is often useful to examine the corroded metal in two stages: first with the corrosion products still adhering to the metal, and again after removal of the corrosion products.

Darrin (1946), from experience with ferrous and non-ferrous metals has devised a system in which a score is allocated for the uncleaned specimen on the following basis:

Discoloration--none (3), slight (2), moderate (1), bad (0).
Roughening--none (4), slight (3), moderate (2), bad (0).
Local Corrosion--none (9), slight (6), moderate (3), bad (0).
Depth of Pits--0.001 in. (12), 0.001 in to 0.004 in. (9), 0.005 in. to 0.014 in. (6), 0.015 in. to 0.030 in. (0).
General corrosion--none (12), slight (9), moderate (6), bad (3), very bad (0).
Maximum total score--40.

The condition of the corrosive liquid is similarly scored:

Cloudiness--none (4), slight (3), moderate (2), bad (0).
Precipitate--none (8), slight (5), moderate (2), bad (0).
General appearance--good (8), fair (6), poor (4), bad (2), very bad (0).
Maximum total score--20.

In addition to the individual assessment of the particular features of corrosion, the over-all condition of a given specimen is expressed as a percentage of the possible maximum (40), while the over-all condition of the system is expressed as a percentage of the possible maximum for the sum of the liquid and the specimens in the system. The percentages are interpreted as shown in Table 8. After the specimen is cleaned the relative order of severity of the different types of corrosion, the maximum pit depth, and the number of pits per unit area are noted. Apart from the depth of pitting, no guide is given as to the meaning of the terms of severity of the corrosion involved in the system.

Table 8. Interpretation of scores according to Darrin (1946).

Score, %	Designation	Degree of Corrosion
100	Perfect	No indication
95-99	Excellent	Minor, but very satisfactory
85-94	Good	Definite, but probably satisfactory
75-84	Fair	Questionable
65-74	Poor	Probably unsatisfactory
64	Bad	Severe corrosion

Two laboratory procedures which have been employed or recommended for investigations of this nature follow:

The ASTM (1958) has published a standard method of total immersion corrosion testing for soak tank metal cleaners. Described is the scope of the test, apparatus, test specimens, precleaning test specimens (degreasing only), test conditions, procedure for quantitative weight loss test (with corrosion products removal methods for different metals listed in appendixes), procedure for qualitative surface corrosion test, procedure for residual-cleaner corrosion test, and reporting the results.

A brief description of the various aspects of the test method follows. The method of testing is intended as a means of determining the corrosive effects of soak tank metal cleaners on all metals other than aluminum and its alloys, under conditions of total immersion, by quantitative measurement of weight change and/or by qualitative visual determination of change. The test is stated as being designed for the determination of the effects of the cleaner on metals being cleaned, and is not for determination of the life of the cleaner or of the containing equipment.

The apparatus consists of test tubes, Allihn-type condensers, with stoppers or joints and a constant temperature device. The representative test specimens should have an area between 0.300 to 0.375 dm^2. At least two, and preferably four, replicates are recommended to be tested in each concentration of cleaner solution. The precleaning procedure recommended is as follows: (1) Immerse the test specimens in a beaker of carbon tetrachlorice or trichloroethylene and swab the surfaces of the individual specimens thoroughly using clean forceps to hold both the cotton swab and test specimen. (2) Shake off excess solvent and transfer to the vapor degreasing bath long enough to observe the vapor completely covering and condensing on the specimen. (3) Swab the specimen separately in a beaker of alcohol at 50°C (122°F) and shake free from excess alcohol. (4) Transfer the specimens to a beaker of distilled water at 50°C (122°F), swab and shake free of excess water. (5) Immerse the specimens separately several times in the beaker of acetone, and shake free of acetone. Dry in a vacuum desiccator or in a low temperature oven at 37°C (99°F) and weigh.

The recommended test conditions are as follows: The ratio of metal area to solution volume should not be less than 1.5 dm^2/l. The solution concentrations to be tested when the manufacturer's recommendations are available are the following relative concentrations; one-half the concentration recommended, the concentration recommended, and twice the concentration recommended. It was recommended further that a blank test of either two or four replicates in freshly boiled distilled water be included. Freshly boiled distilled water was recommended for making the other water-soluble cleaner solutions. With the available temperature recommendations it was recommended that the tests be conducted at the average recommended temperature and at 11 ± 1°C (20 ± 2°F) above and below this temperature.

The remaining procedure for quantitative weight loss is that after having obtained the initial specimen weight to the nearest 0.001 g the specimen is transferred to the test tubes containing the preheated cleaner solutions. After exposure for a 2 hour period or other appropriate time the specimens are removed from the solution and treated as follows: (1) Hold the specimen in forceps and rinse thoroughly in a 1-liter beaker into which tap water is flowing rapidly. (2) Rinse thoroughly in distilled water at room temperature. (3) Rinse with a stream of acetone from a wash bottle. Shake free from acetone and dry. (4) Examine specimen appearance before and after removal of corrosion products with regard to the following: Discoloration, Dulling, Etching, Presence of accretions and relative amounts and areas, Type of pitting--wide, medium, or narrow, and Presence of selective or localized attack. (5) Corrosion products may be removed from iron and steel by chemical treatment in a boiling solution of ammonium citrate (10 percent by weight) with a 2 or 3 minute immersion time.

Shaw and McCallion (1959) of Chas. Pfizer and Company, Inc., manufacturer of a sodium gluconate compound which is used in combination with caustic systems as a sequestering agent for water hardness encountered in bottle washing, conducted a study of the corrosiveness of gluconate-caustic systems. Their paper and additional correspondence with McCallion (1959) indicate the laboratory procedure used. The laboratory test method involved the use of a standard roller, bushing and pin obtained from a well-known chain manufacturer. The bushing, pin and roller were thoroughly cleaned in detergent solution and rinsed. Any residual scale or rust was removed by a short dip in 5 percent ammonium citrate solution at about 65°C (150°F), followed by rinsing, drying and weighing. Specimens were assembled and placed in 500 ml polyethylene bottles, (the metal surface area was 195 cm^2 in a test solution volume of 200 ml, the roller contributing 125 cm^2). The pin was externally connected to a motor and rotated at 25 RPM, which is the equivalent of a roller linear speed of approximately 16 ft/min. The roller remained stationary. Test solutions of 3 percent sodium hydroxide plus additives were prepared using water of 12 grains per gallon hardness. The addition of gluconate to the solutions varied from 0.045 to 0.15 percent based on the total solution weight. Various other additives were also used. The test solutions were added to individual bottles which were then placed in a constant temperature bath at 60°C (140°F). The length of exposure was for 7 days. Most of the tests were for a single 7-day exposure. A few tests were for two 7-day exposures. The weight loss of only the bushing and pin was determined, because as the authors pointed out the roller was so heavy as to make its weight loss inaccurate for data conversion. The specimens were then treated with a dilute acid dip (2 percent hydrochloric acid plus Rodine inhibitor) for 2 to 5 minutes to insure removal of any residual scale. The specimens were then rinsed, dried, and weighed again. It was stated that, "since the differences in weight before and after the dilute acid treatment were negligible, the weight losses prior to the dilute acid treatment were used in calculating corrosion rates. The acid treatment was however, continued throughout the test."

In addition to measured weight losses, iron analysis of each test solution was performed. They stated that this provided a check of corrosion figures. They said that the corrosion figures based on the two different data agreed in 13 out of 15 runs, which was said to be well within the range of experimental error. It is interesting to note that this close agreement was obtained in the iron analysis where the total amount of corrosion due to the bushing, pin, and roller was determined, while in the weight loss measurement the amount of corrosion was determined using only the bushing and pin.

The iron analysis was performed colorimetrically using hydroxylamine to reduce all iron to the ferrous state and adding phenathroline to form the colored ferrous-phenanthroline complex. (Before analysis all insoluble iron in any of the test solutions was dissolved with hydrochloric acid so that the analysis gave total iron removed from the metal.) This would not give the total corrosion since the corrosion products on (or adhering to) the metal were not included in this iron analysis as described above.

An appropriate statement at this point seems to be one made by Fontana (1960) at the end of his paper on corrosion testing. He stated that, "in conclusion, I should like to state that hundreds of different types of corrosion tests are made. Apparently the type and detail are limited only by the ingenuity of the personnel involved. Types vary from the 'quick and dirty' to exotic arrangements. The important point is that the test should produce data suitable for the intended use or application."

RESULTS AND DISCUSSION OF TESTS PERTAINING TO THE DEVELOPMENT OF THE EXPERIMENTAL PROCEDURE

Preliminary tests were conducted to become familiar with the techniques and essential details commonly employed in total immersion corrosion studies. Tests were conducted to obtain acceptable processes for pickling and removal of corrosion products from corrosion test specimens. Certain processes either recommended for use or used in previous studies reported in the literature were evaluated for use in this study. Since each test is an entity in itself, it will be treated as such as far as possible.

A preliminary test was conducted as follows in order to become acquainted with and to facilitate an appreciation for the various techniques and details required in corrosion evaluations: Pint Mason jars with glass covers were used, each jar containing about 450 ml of cleaning solution under study and one hot-rolled mild steel specimen (0.25cm x 4.0 cm x 8.0 cm). Prior to use, the specimens were washed in a household detergent solution (Tide), rinsed in water, wiped dry, dried in a vacuum oven and weighed to the nearest 0.0001 g. The specimens were placed in the jars and laid at about a 45 degree angle to the base of the jar. At the end of the exposure period, the specimens were removed from the jars and again washed, rinsed, dried, and weighed as before.

The data obtained for duplicate specimens and repeated immersions were obviously neither reliable or reproducible. The apparent reasons for this are probably one or more of the following: (1) The washing procedure may have been inadequate. (2) Presence of and variations in the amount of scale already on the surface could have interfered with corrosion and the obtaining of reproducible results. (3) Since the strip laid at an angle, corrosion products might have accumulated more on one surface than on the other, thus influencing corrosion. (4) The washing procedure employed after exposure did not facilitate the removal of corrosion products, leaving them to interfere with subsequent corrosion. (5) Glass containers were used with alkaline cleaning solutions, and changes in solution corrosiveness could occur, due to exhaustion of corrosive constituents, or the accumulation of constituents that might affect further corrosion. Several jars broke during the test.

A second test was conducted as follows: Polyethylene containers and caps with nylon string attached to the cap for support of one hot-rolled mild steel specimen (0.25cm x 4.0 cm x 8.0 cm) in 500 ml of cleaning solution were used. Prior to use the surface of the specimens were milled down to base metal, degreased according to a standard procedure given in ASTM (1958), rinsed, dried in a vacuum desiccator and weighed to the nearest 0.0001 g. The specimens were suspended from the caps in containers of solution for exposure. During exposure of the specimens a test using control specimens was conducted to evaluate the acceptability of a corrosion products removal method suggested in the Appendix of an ASTM (1958) standard. The method was considered unsatisfactory for use, since considerable base metal was removed from the specimens. (The results of this test and others to develop a satisfactory corrosion products removal procedure without appreciable removal of base metal are presented later in this section.) As a result, this test had to be terminated with an unsatisfactory method for removal of corrosion products and the results are therefore not presented. However, the results obtained did appear to be more reliable and reproducible than those of the previous test.

Two important problems remain to be dealt with. First, the removal of surface scale and oxides which vary in amount, so as to obtain a uniform, reproducible surface for the determination of corrosion. A chemical treatment would be advantageous compared with the rather time consuming and expensive milling process to remove surface scale and oxides used in the above test. Second, an acceptable corrosion products removal process (one that effectively and efficiently removes corrosion products with a minimum removal or attack of base metal) is needed.

Tests to obtain acceptable processes for the removal of surface scale before exposure and the removal of corrosion products after exposure follow:

It was pointed out in the literature review that Shaw and McCallion (1959) used a short dip in an ammonium citrate solution (5 percent by weight) at 65°C (150°F) to remove scale and rust before exposure of their specimens. This pickling process was evaluated for use in this study as follows: Prior to pickling, hot and cold rolled mild steel specimens were first measured to facilitate calculation of the surface area, then degreased according to the procedure given in ASTM (1958) standard, dried in a vacuum oven and weighed. After pickling the specimens for 2 minutes they were rinsed, dried and weighed. The mean weight loss of duplicate hot and cold rolled mild steel specimens was 21.7 mg/dm^2 and 4.2 mg/dm^2, respectively. A visual examination of the specimens indicated that the cold rolled specimens were adequately treated, however, there appeared to be some dulling of the metal finish. This treatment was inadequate for hot rolled specimens, since there was little removal of the heavy scale deposits present initially.

Acid solutions are commonly used for pickling specimens as pointed out in the literature review. The use of inhibitors has also been recommended to retard the action of the acid on the base metal. Rodine inhibitors are recommended for this purpose.

Rodine III inhibitor was obtained from a local chemical supplier and used with hydrochloric acid as recommended for pickling mild steel specimens as follows: The specimens used in the previous test were immersed for 2 minutes in a 65°C (150°F) solution of 2 percent hydrochloric acid (by weight) plus 0.02 percent Rodine III (by weight), rinsed, dried, weighed and visually examined and then this same process was repeated again. The mean weight loss of duplicate cold rolled mild steel specimens was 5.6 and 6.9 mg/dm^2 after the first and second treatments, respectively. The mean weight loss of duplicate hot rolled mild steel specimens was 178.2 and 166.4 mg/dm^2 after the first and second treatments, respectively. The scale deposits on the hot rolled specimens had loosened up and some rubbed off on the forceps used in handling them after the first treatment. Most of the scale, but not all, was removed after the second treatment. These results indicated that an inhibited acid pickling solution of higher concentration, and/or higher temperature could be satisfactory. Another test was conducted using the same type inhibited acid pickling solution, at boiling temperature with a 2 minute immersion on new degreased hot rolled specimens. The mean weight loss of the duplicate specimens was 428.3 mg/dm^2. The specimens were microscopically examined after 1 minute and 2 minutes in the solution. After 1 minute the surfaces were free of scale and no further change in the surface was noted after the second minute of immersion. The results of this and the previous test showed that this solution (2 percent hydrochloric acid (by weight) plus 0.02 percent Rodine III (by weight)) would be satisfactory for pickling hot and cold rolled mild steel specimens. However, correspondence with Linden (1960) of the Amchem Products, Inc., producers of the Rodine inhibitors, resulted in the recommendation that Rodine 213 be used in preference to Rodine III because Rodine 213 is a more efficient, stronger, heat stable product.

The following test was conducted using Rodine 213 as the inhibitor. Duplicate hot and cold rolled mild steel specimens were measured, degreased, dried and weighed. The specimens were then immersed and brushed for 2 minutes in a 93°C (200°F) solution of 15 percent hydrochloric acid (by weight) plus 0.4 percent Rodine 213 (by volume), rinsed, dried and weighed. The mean weight loss of the duplicate hot and cold rolled specimens was 354.7 mg/dm^2 and 3.3 mg/dm^2, respectively. Examination of the specimens after pickling showed that the scale had been removed. Successive immersions of duplicate hot rolled mild steel specimens after this first pickling treatment showed the following mean weight losses: 1.7, 1.5,1.6, and 1.4 mg/dm^2 when pickled exactly as described above a second, third, fourth and fifth time. These results further indicated the complete removal of scale in the first treatment, and also that once the scale has been removed that very little attack on the base metal occurs.

The weight loss due to this pickling process was also evaluated when hot and cold rolled mild steel specimens were prepared for a study to determine if the amount of corrosion in several cleaning solutions was significantly different for these two types of specimens. The results of this test are reported later. The mean weight loss and standard deviation for 16 hot and 16 cold rolled AISI No. C 1008 steel specimens due to pickling was 385.8 mg/dm^2 and 21.6 mg/dm^2 and 3.6 mg/dm^2 and 1.4 mg/dm^2, respectively. Since this pickling process was both effective and efficient, and did not result in appreciable attack of the base metal it was accepted for use in these corrosion studies.

With an acceptable pickling process specimens can be prepared and immersed in the respective solutions for corrosion rate evaluations. After immersion the corrosion products must be completely removed, with a minimum removal of base metal before assessing the amount of corrosion by weight loss. It is important to point out that the weight losses are not expected to be large, and therefore, drastic methods (those which remove considerable base metal) can not be used. The effect of several processes used for corrosion products removal, on base metal of iron and steel specimens is reported in the literature. They are presented below to provide an indication of what might be expected. Champion (1952) reports that immersion of steel in 20 percent sulphuric acid solution containing 0.05 percent di-orthotolylthiourea as inhibitor for 1 hour at 60°C (140°F) resulted in 13 g/m^2 (130 mg/dm^2) metal loss. He also reports that immersion of blank specimens in 20 percent ammonium citrate solution for about 20 minutes at 75 to 80°C (167 to 176°F) resulted in a weight loss of less than 3 g/m^2 (30 mg/dm^2). Knapp (1948) shows weight losses ranging from 0.0 to 6.0 mg/dm^2 for a number of clean metals subjected to electrolytic cleaning in inhibited 5 percent sulfuric acid at 75°C (167°F) for 3 minutes.

It is essential as pointed out by Champion (1952), ASTM (1952) and Knapp (1948) that regardless of the method of removing corrosion products, the rate of base metal removal must be determined for the particular materials under test, in order to avoid major errors.

The ASTM (1958) and Speller (1935) have suggested that the corrosion products on iron and steel be removed by immersing the specimens for 2 minutes in a boiling solution of ammonium citrate (10 percent by weight). This process was evaluated as follows: Duplicate hot rolled mild steel specimens which had been milled to remove the scale and expose the base metal, were measured, degreased, dried, and weighed. They were then given the above corrosion product removal treatment, rinsed, dried, and weighed. The mean weight loss of the duplicate specimens after each of 4 consecutive treatments was 9.5, 6.1, 6.1 and 5.0 mg/dm^2. Another test was conducted exactly as described above using 5 percent ammonium citrate at 65°C (150°F) and boiling to determine if a decrease in concentration at the same temperature or if a decrease in both concentration and temperature would appreciably decrease the amount of base metal removed. The mean weight loss of duplicate specimens after each of 4 consecutive treatments was 5.6, 4.7, 4.9 and 5.1 mg/dm^2 with the boiling solution, and 4.2, 4.3, 4.6 and 3.5 mg/dm^2 with the 65°C (150°F) solution.

Since considerable base metal was still being removed, a change was made to the use of an inhibited acid solution for corrosion products removal. Evans (1960) has pointed out that inhibited acid is generally recommended for corrosion products removal and that preliminary experiments are necessary to find the solution and lowest concentration which is effective without seriously attacking the base metal. Knapp (1948) suggests some inhibitors for use, one of these was Rodine. To evaluate this process, duplicate milled (to remove scale and expose base metal) specimens were measured, degreased, dried and weighed. They were then immersed for 2 minutes in 2 percent hydrochloric acid (by weight) plus 0.02 percent Rodine III (by weight) solution. The mean weight loss of the duplicate specimens after each of 4 consecutive treatments was 10.5, 10.9, 11.8, and 17.1 mg/dm^2 in boiling solution, and 3.1, 2.7, 4.2, and 2.3 mg/dm^2 in 65°C (150°F) solution. The over-all mean weight loss of the 4 consecutive treatments in the 65°C (150°F) solution was about 25 percent less than the 5 percent ammonium citrate solution at 65° (150°F).

An additional test was conducted exactly as described above except that 0.04 percent RodineIII was used in a solution at 65°C (150°F) to determine if the amount of metal removed could be reduced still further. The mean weight loss of duplicate specimens after each of three consecutive 2-minute immersions in 65°C (150°F) solution of 2 percent hydrochloric acid plus 0.04 percent Rodine III was: 2.2, 2.7, and 1.4 mg/dm^2. The over-all mean of these 3 immersions' weight losses is about 32 percent below the over-all mean of the 4 immersions' weight losses in the previous inhibited acid solution at 65° (150°F) and about 50 percent below the mean of the 4 immersions' weight losses in the 5 percent ammonium citrate at 65°C (150°F).

As mentioned earlier in the section on obtaining an acceptable pickling process, Linden (1960) suggested the use of Rodine 213 in preference to Rodine III because it is a stronger, more efficient, and heat stable inhibitor. Their literature showed that the maximum amount of base metal removed from mild steel immersed in a 5 percent (by weight) hydrochloric acid plus 0.1 percent (by volume) Rodine 213 solution at 82°C (180°F) would be about 0.17 mg/dm^2-min. A solution of 5 percent hydrochloric acid (by weight) plus 0.1 percent Rodine 213 (by volume) was evaluated for its effect on base metal as follows: Hot and cold rolled AISI No. C 1008 steel specimens were measured, degreased, pickled (using the pickling process adopted above), rinsed, dried, and weighed. They were then immersed and brushed, in the above solution at 82°C (180°F) for 2 minutes. The mean weight loss of duplicate specimens after each of 6 consecutive treatments was as follows: 1.7, 1.7, 1.9, 1.8, 1.8, and 1.6 mg/dm^2 with cold rolled steel and 2.0, 2.1, 1.7, 1.7, 2.0 and 1.6 mg/dm^2 with hot rolled steel.

A comparison of the mean and standard deviation of each of the better processes of each type evaluated above follows: The 5 percent ammonium citrate solution at a temperature of 65°C (150°F) and a 2 minute immersion of the specimens resulted in an over-all mean base metal removal of 4.1 mg/dm^2 and a standard deviation of 0.50 mg/dm^2. The 2 percent hydrochloric acid plus 0.04 percent Rodine III solution at 65°C (150°F) and with a 2 minute specimen immersion had an over-all mean base metal removal of 2.1 mg/dm^2 and a standard deviation of 0.58 mg/dm^2. The 5 percent hydrochloric acid plus 0.1 percent (by volume) Rodine 213 solution at 82°C (180°F), with a 2-minute immersion of both cold rolled and hot rolled AISI No. C 1008 steel specimens resulted in an over-all mean base metal removal of 1.7 mg/dm^2 and standard deviation of 2.4 mg/dm^2 for the cold rolled specimens and a mean base metal removal of 1.8 mg/dm^2 and a standard deviation of 0.26 mg/dm^2 for the hot rolled specimens. Since the latter process resulted in a minimum removal of base metal (small mean) and a small deviation in weight loss for consecutive treatments (small standard deviation) it was adopted for use in this corrosion study.

The results of a direct comparison of the corrosion products removal method suggested by the ASTM (1958) and the one to be used in this study follows: Eight cold rolled AISI No. C 1008 steel specimens were measured, degreased, pickled, rinsed, dried and weighed. Four specimens were immersed for 2 minutes in a boiling solution of 10 percent ammonium citrate, and the other 4 specimens were immersed for 2 minutes in 82°C (180°F) solution of 5 percent hydrochloric acid plus 0.1 percent Rodine 213, then rinsed, dried and weighed. This procedure was repeated three times with the inhibited acid solution and six times with the ammonium citrate solution. The mean weight loss after each treatment was 2.0, 1.9, and 1.9 mg/dm^2 with the inhibited acid solution, and 8.4, 5.8, 3.5, 4.2, 4.0 and 3.5 mg/dm^2 with the ammonium citrate solution. The combined over-all mean weight loss and standard deviation (based on the individual weight loss values for each specimen) of the inhibited acid and ammonium citrate were 1.9 mg/dm^2 and 0.14 mg/dm^2 and 4.9 mg/dm^2 and 2.1 mg/dm^2 respectively. The data show that the inhibited acid removes about 61 percent less base metal with about a 93 percent less deviation from specimen to specimen than the ammonium citrate solution.

CORROSION STUDIES

THE EXPERIMENTAL PROCEDURE

Laboratory total immersion corrosion tests were conducted to assess the corrosiveness of alkaline sequestering agents to mild steel specimens. The amount and intensity of corrosion was determined by weight loss measurement and visual examination. The experimental procedures used are grouped according to: Metal, Corrosion media, Laboratory exposure conditions, or Assessment of effects on the metal and media.

Metal factors

Commercial quality AISI No. C 1008 cold rolled and hot rolled steel plate corrosivity was determined in several alkaline solutions representative of those to be studied in this investigation. No significant difference in corrosivity was found for cold rolled and hot rolled steel specimens when immersed in distilled water solutions of 3% sodium hydroxide, 3% sodium hydroxide plus 0.168% sodium gluconate and 3% sodium hydroxide plus 0.24% ethylenediaminetetraacetic acid; therefore, cold rolled steel specimens were used throughout the remainder of the investigation. Test specimens of about 1 mm in thickness, 3 cm in width and 10 cm in length were furnished by the U. S. Steel Corporation with the detailed chemical analysis given in Table 9. The microstructures of both materials were normal for C 1008 steel.

Table 9. Composition of hot rolled and cold rolled AISI No. C 1008 steel specimens.

Materials	ARL No.[1]	Composition, weight percent							
		C	Mn	P	S	Si	Cu	Ni	Cr
Hot rolled steel	L 1746	0.083	0.37	0.013	0.028	0.012	0.037	0.003	0.018
Cold rolled steel	L 1747	0.057	0.34	0.007	0.024	0.006	0.001	0.003	0.01

[1] ARL = Applied Research Laboratories Of U. S. Steel Corporation

Preparation of the specimens involved drilling a hole 1 mm in diameter at the end of each specimen (to be used in supporting the specimen), measurement of each specimen's dimensions with vernier calipers to 0.1 mm (the specimens generally measured about 1.3 mm in thickness, 4.15 cm cm in width, and 10.17 cm in length giving a surface area of 88.13 cm^2 and having an initial weight of about 44.4523 g), and degreasing and pickling of the specimens. The specimens were degreased according to the following procedure recommended in the ASTM (1958) standard method of total immersion corrosion testing for soak tank metal cleaners: (1) Immerse the test specimens in a beaker of carbon tetrachloride or trichloroethylene and swab the surfaces of the individual specimens thoroughly using clean forceps to hold both the cotton swab and test specimen. (2) Shake off excess solvent and transfer to the carbon tetrachloride or trichloroethylene vapor degreasing bath long enough to observe the vapor completely covering and condensing on the specimen. (3) Swab the specimen separately in a beaker of alcohol at 50°C (122°F), and shake free from excess alcohol. (4) Transfer the specimens to a beaker of distilled water at 50°C (122°F), swab and shake free of excess water. (5) Immerse the specimens separately several times in the beaker of acetone, and shake free of acetone. After degreasing, the specimens were pickled to remove surface scale and provide a uniform, reproducible surface. The specimens were immersed and brushed with a nylon bristle brush for 2 minutes in a 93°C (200°F) solution of 15 (weight) percent hydrochloric acid plus 0.4 (volume) percent Rodine 213, rinsed and weighed. Two specimens were pickled in each beaker containing 500 ml of pickling solution. The specimens were rinsed for one-half minute in each of two 1-l. beakers of distilled water, followed by an acetone rinse from a wash bottle. They were then wrapped in a dry, smooth, hard-surface paper and dried for an hour in a vacuum desiccator. After immersion in corrosion media, the specimens were removed and rinsed as described above.

Next, it was necessary to remove the corrosion products before weighing and subsequent re-immersion of the specimens. (Four replicates were used for 5 consecutive immersions with the weight loss determined after each of the five 7-day immersions in order to evaluate each treatment effect.) The corrosion products were removed by a 2-minute immersion of the specimens in 5 (weight) percent hydrochloric acid plus 0.1 (volume) percent Rodine 213 solutions at 82°C (180°F). Two specimens were processed in each 500 ml beaker of corrosion product removal solution. The specimens were then rinsed, dried and weighed as described above.

Corrosion media

Boiled distilled water and water with 12 grains per gallon total hardness as calcium carbonate were used to prepare corrosion media. The hard water was prepared by diluting tap water of 19 grains per gallon total hardness with distilled water. The hard water of 12 grains per gallon total hardness consisted of 8 grains per gallon as calcium hardness and 4 grains per gallon as magnesium hardness. The iron and chlorine content were each less than 1 ppm.

Water, sodium hydroxide, sodium gluconate, sodium versenate (tetrasodium ethylenediaminetetraacetate), trisodium phosphate, and tetrasodium pyrophosphate were used as agents in this corrosion investigation. The manner in which these agents were used is described in Figure 7; the agent combinations are: water; 3% sodium hydroxide; 3% sodium hydroxide plus sodium gluconate; 3% sodium hydroxide plus sodium versenate (tetrasodium ethylenediaminetetraacetate); 3% sodium hydroxide plus trisodium phosphate (TSP); and 3% sodium hydroxide plus tetrasodium pyrophosphate (TSPP). Concentrations of the agents can also be noted on Figure 7. Three concentrations of sodium gluconate and sodium versenate (tetrasodium ethylenediaminetetraacetate) were evaluated; these are the calculated theoretical amounts of the chemical necessary to sequester the hardness in 12 grains per gallon, water, two times this amount and four times this amount, which correspond to the 1x, 2x, and 4x values in Figure 7. One concentration of trisodium phosphate and tetrasodium pyrophosphate was evaluated. This concentration was the commercial recommended amount which is approximately two times the theoretical concentration for 12 grain per gallon water. The specific amounts of each agent added on a percent by weight basis is given with the results (Table 26). The amount of sequestering agent added is based on the amount of water and not on the total solution weight.

The entire experiment diagrammed in Figure 7 was carried out for distilled water and for hard water of 12 grains per gallon total hardness. When the distilled water was used, the agents and concentrations were the same as with hard water. Since the sequestering agents are added to control hardness, the unreacted sequestering agent in the distilled water test is at a higher concentration than in the hard water tests.

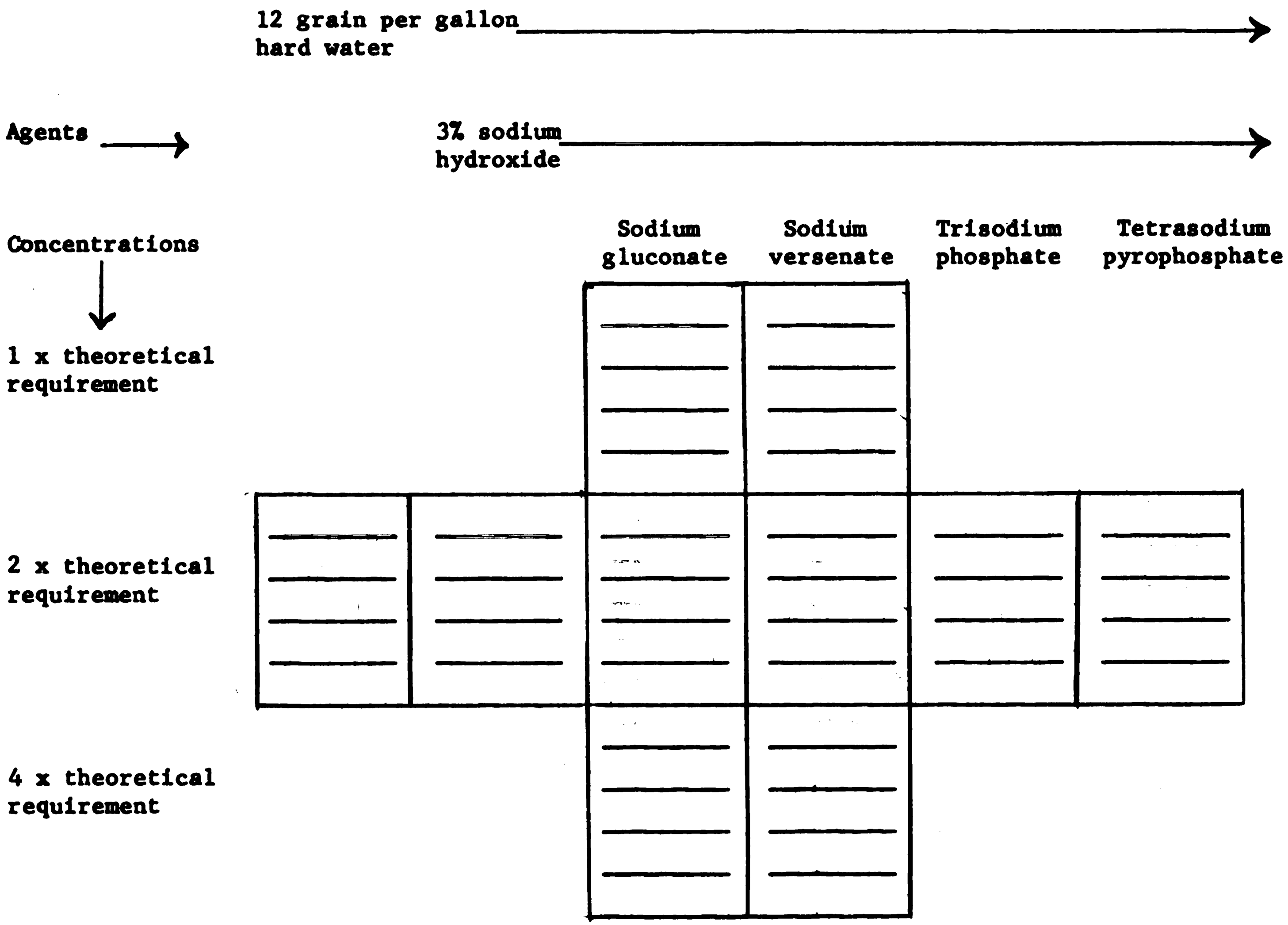

Fig. 7. Corrosion experiment

Laboratory exposure conditions

The specimens were tested in 500 ml polyethylene bottles. The specimens were supported by a nylon string attached to the plastic bottle closure with epoxy resin; one specimen to a bottle. This method of suspending the specimens prevented them from touching the container. The ratio of solution volume to specimen surface area was 5.68 ml/cm^2 (or 500 $ml/88cm^2$).

The majority of the tests were carried out at 150 ± 1°F in an automatic temperature controlled agitated water bath. (The water in the bath was agitated and not the bath or the test solutions.) Tests limited to one agent concentration in distilled water were carried out at 130°F and 170°F. All test solutions were preheated to the desired temperature before adding the test specimens to the bottles.

All tests were replicated four times. The lines in Figure 7 illustrate the replicated samples. The tests were repeated for five consecutive 7-day immersions to determine corrosion variation with successive immersion. Fresh test solution was added to cleaned bottles after each immersion.

Assessment of corrosion effects on the metal and media

The effects of corrosion on the steel specimens tested were determined after each immersion by weight loss and by subjectively observing the change in the appearance of the specimens. The specimens were weighed to 0.1 mg on a laboratory analytical balance having a sensitivity of 0.05 mg at full load. The corrosion results are reported as milligrams weight loss per square decimeter-week (mg/dm^2-week). After removal of the test specimens from the test solutions and rinsing, the appearance and general nature of corrosion was assessed by visual examination of the test specimens, both before and after removal of corrosion products. The specimens and test solutions were examined and scored according to a system developed by Darrin (1946), with the exception of one modification. All categories used for assessing the visual specimen corrosion involved a qualitative measure or type of score with the exception of the pitting category. Darrin's procedure requires a quantitative measure of pit depth and the score given was bases on this pit depth. In this investigation pit depth was not measured, but rather pitting was given a qualitative score based on the amount and intensity of pitting. Darrin's system for visual examination and scoring of the specimens and solutions follows:

> System for visual examination and scoring of the corrosion effects on the test specimens before and after removal of corrosion products:
>
> Discoloration--none(3), slight (2), moderate (1), bad (0).
> Roughening--none (4), slight (3), moderate (2), bad (0).
> Local corrosion--none (9), slight (6), moderate (3), bad (0).
> Pitting--none (12), slight (9), moderate (6), bad (3), very bad (0).
> General corrosion--none (12), slight (9), moderate (6), bad (3), very bad (0).
> Maximum total score--40.
>
> System for visual examination and scoring of the corrosion effects on the test solutions:
>
> Cloudiness--none (4), slight (3), moderate (2), bad (0).
> Precipitate--none (8), slight (5), moderate (2), bad (0).
> General appearance--good (8), fair (6), poor (4), bad (2), very bad (0).
> Maximum total score--20.

In addition to the assessment of the particular features of corrosion, the over-all condition of the specimens or solutions given a particular treatment are expressed as a percentage of the possible maximum; while the over-all condition of the system is expressed as a percentage of the possible maximum for the sum of the liquid and the specimens in the system. The percentages are interpreted in accordance with the following table:

Table 10. Interpretation of scores according to Darrin (1946).

Score, %	Designation	Degree of corrosion
100	Perfect	No indication
95-99	Excellent	Minor, but very satisfactory
85-94	Good	Definite, but probably satisfactory
75-84	Fair	Questionable
65-74	Poor	Probably unsatisfactory
64	Bad	Severe corrosion

In presenting the above experimental procedures a number of the tests conducted in this investigation have been mentioned. In addition to these, the reproducibility of the above experimental procedure with different individuals was determined. The variation in corrosion with length of immersion for several agents was assessed. The effect of a wetting agent on the corrosiveness of an alkaline sequestering agent solution was determined. The corrosiveness of aqueous sequestering agent solutions was also determined.

RESULTS AND ANALYSES

This investigation is concerned with detergent solution corrosion of equipment used in cleaning reusable beverage containers, and in particular, sequestering agent corrosion of bottle washing machines. The results of this investigation are reported according to the following phases of study: (1) Studies on materials and methods, (2) Studies on distilled water-sequestering agent systems, (3) Studies on distilled water-sodium hydroxide-sequestering agent systems, (4) Studies on hard water-sodium hydroxide-sequestering agent systems, and (5) Distilled water and hard water studies combined and compared. It should be noted that these studies are not necessarily presented in the order in which they were conducted, but rather according to an order which tends to facilitate their discussion.

Studies on materials and methods

Materials

The results of a test to determine if cold rolled and hot rolled AISI No. C 1008 steel used in beverage bottle washing equipment varies in susceptibility to corrosion, as measured by weight loss after each of three immersions of separate replicate sets of specimens in four detergent solutions, similar to those to be evaluated in this study, are presented in Tables 11 and 12. The mean and standard deviation for each detergent by each immersion and steel are included in these tables. (The means and standard deviations are for 4 replications in these tables and all subsequent tables.) The variances calculated from the standard

Table 11. Corrosion weight loss data of steel specimens immersed in distilled water for one week (7 days).

Steel, AISI No. C 1008		Weight loss, mg/dm^2-week			
		Immersions			Steel, over-all means
		1	2	3	
Cold rolled	Mean	128.87	144.63	151.96	141.82
	Standard deviation	3.70	4.86	5.02	
Hot rolled	Mean	117.54	143.03	131.87	130.81
	Standard deviation	6.28	6.90	6.16	
Immersion over-all means		123.20	148.83	141.91	136.31

Table 12. Corrosion weight loss data of steel specimens immersed in alkaline detergent solutions for one week (7 days).

Agents	Weight loss, mg/dm^2-week								
	Steel, AISI No. C 1008								
	Cold rolled				Hot rolled				
	Immersions			Agent over-all means	Immersions			Agent over-all means	Grand agent over-all means
	1	2	3		1	2	3		
Sodium hydroxide									
Mean	2.88	3.15	3.47	3.17	2.76	2.82	3.27	2.95	3.06
Standard deviation	0.20	0.33	0.28		0.17	0.57	1.25		
3% Sodium hydroxide + 0.168% sodium gluconate									
Mean	4.54	3.37	3.42	3.78	4.87	2.78	3.16	3.60	3.69
Standard deviation	0.54	0.53	0.24		0.69	0.61	0.20		
3% Sodium hydroxide + 0.24% ethylenediamine-tetraacetic acid									
Mean	3.14	5.99	4.01	4.38	3.03	5.54	4.27	4.28	4.33
Standard deviation	0.44	1.04	0.40		0.59	1.06	0.71		
Immersion over-all means	3.52	4.17	3.64		3.55	3.71	3.57		
Steel over-all means				3.78				3.61	3.69

deviations in Table 11 and Table 12 were tested for homogeneity of variance using Cochran's Test (Dixon and Massey, (1957). Homogeneity of variance was found at the 5% level of significance in both cases; thus satisfying the requirement for homogeneity of variances, essential to the use of analysis of variance methods.

The results of an analysis of variance of the cold and hot rolled steel specimens weight loss data obtained after immersions in distilled water are presented in Table 13. The interaction was significant (5% probability level of significance) and main effects were highly significant (1% probability level of significance). The interaction is shown graphically in Figure 8. The error mean square was used to calculate estimates of the standard errors. The estimate of the standard error for the steels (S_s) was 1.62 mg/dm^2-week and for the immersions (S_I) was 1.98 mg/dm^2-week. The difference between steel over-all means was highly significant as shown by the F value (see Table 13). Cold rolled steel suffered more corrosion than hot rolled steel. The immersion over-all means were tested for significance by Harter's (1960) critical values for Duncan's new multiple range test. (This method of testing for significant differences is used in the remaining analyses.) Significantly more corrosion was found in immersions two and three than in immersion one. The amount of corrosion was not significantly different for immersions two and three.

Table 13. Analysis of variance of corrosion weight loss data of cold and hot rolled AISI No. C 1008 steel specimens immersed in distilled water.

Source	Degrees of freedom	Sum of squares	Mean square	F
Total	23	3709.71		
Immersions	2	2077.55	1038.77	33.22**
Steels	1	726.99	726.99	23.25**
Interaction	2	342.28	171.14	5.47*
Error	18	562.89	31.27	

*Significant, 5% level.
**Significant, 1% level.

The analysis of variance of the weight loss data presented in Table 12 for cold and hot rolled steel specimens immersed in the alkaline detergent solutions is presented in Table 14. The analysis shows

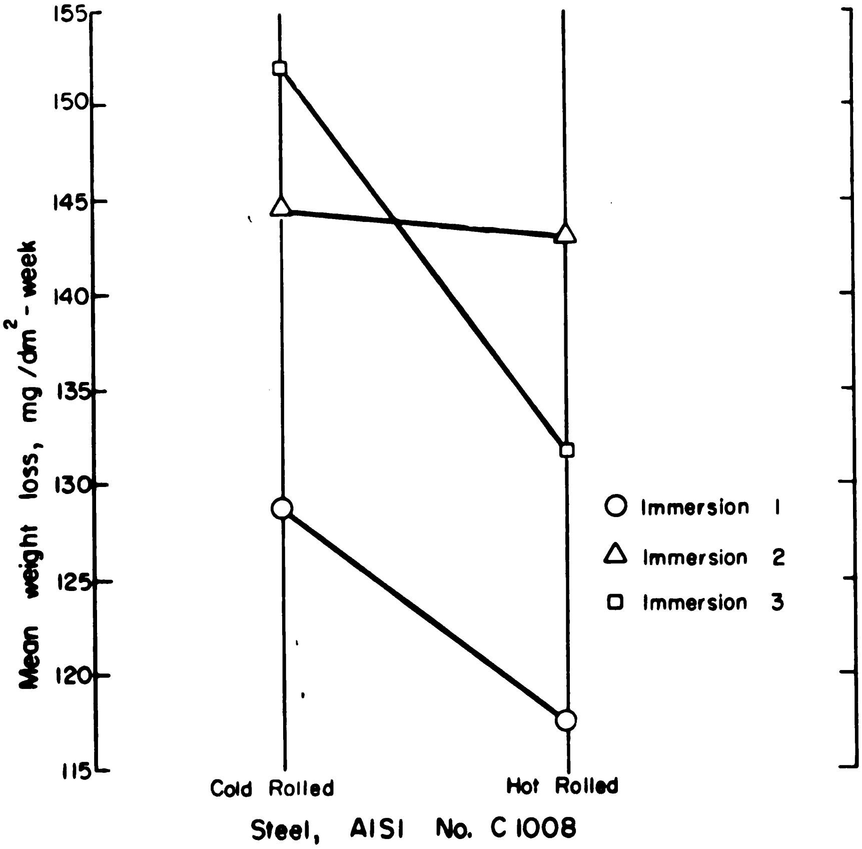

Fig. 8. Immersion-steel interaction with distilled water as corrosive liquid.

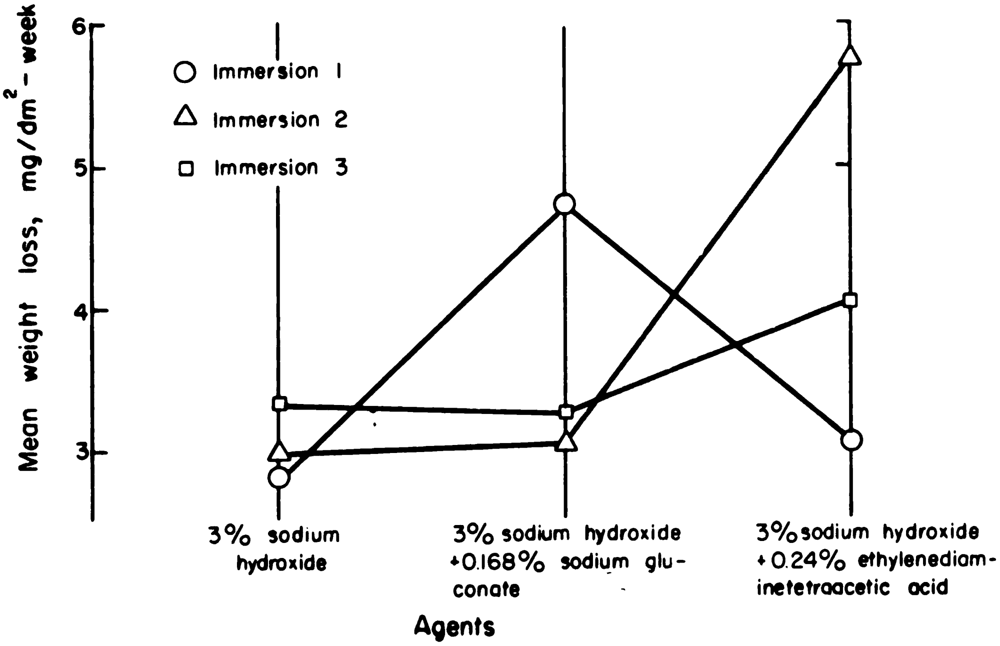

Fig. 9. Immersion-agent interaction with cold and hot rolled steel specimens.

Table 14. Analysis of variance of corrosion weight loss data of cold and hot rolled AISI No. C 1008 steel specimens immersed in alkaline detergent solutions.

Source	Degrees of freedom	Sum of squares	Mean square	F
Total	71	85.16		
Immersions	2	2.26	1.13	2.92
Steels	1	0.485	0.485	1.25
Agents	2	19.46	9.73	25.16**
Interactions				
IxS	2	0.818	0.409	1.06
IxA	4	40.59	10.15	26.24**
SxA	2	0.042	0.021	0.054
IxSxA	4	0.620	0.155	0.401
Error	54	20.88	0.387	

**Significant, 1% level.

that the steel and immersion main effects are not significant, and that the agent main effects and immersion-agent interaction effects are highly significant. The interaction is shown graphically in Figure 9. The grand agent over-all means for 3% sodium hydroxide, 3% sodium hydroxide plus 0.168% sodium gluconate, and 3% sodium hydroxide plus 0.24% ethylenediaminetetraacetic acid are significantly different from each other (given in order of increasing corrosivity).

Visual examination results scored according to Darrin's (1946) system (modified by giving a qualitative score for pitting rather than a quantitative score based on measured pit depths) for the cold and hot rolled steel specimens before and after corrosion products removal are shown in Tables 15 and 16. The visual examination results for the solutions scored according to Darrin's system are shown in Table 17. Included in these tables are percent figures representing the total scores obtained with the specimens or solutions expressed as a percentage of their total possible score. The over-all condition of the system, sum of the solution and the specimens in the system before removal of corrosion products, as a percentage of the possible maximum is presented in Table 18. The results shown in these tables indicate no appreciable difference in visual scores for the cold and hot rolled steel specimens.

Methods

A limited test was conducted to determine if different people would

Table 15. Macroscopic examination of the effects of corrosion on cold rolled AISI No. C 1008 steel specimens. Mean values for three immersions data.

Treatment	Examination	Discoloration	Roughening	Local corrosion	Pitting	General corrosion	Total score	Percent of maximum total score
	Maximum score	3	4	9	12	12	40	100
Distilled water	Before CPR[1]	0	1	9	8	0	18	45
	After CPR[2]	0	3	9	10	3	25	63
3% Sodium hydroxide	Before CPR	2	4	8	12	10	36	90
	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide + 0.168% sodium gluconate	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide + 0.24% ethylenediaminetetraacetic acid	Before CPR	1	4	9	12	8	34	85
	After CPR	3	4	9	12	12	40	100

---

[1] Before CPR (before corrosion products removal).

[2] After CPR (after corrosion products removal).

Table 16. Macroscopic examination of the effects of corrosion on hot rolled AISI No. C 1008 steel specimens. Mean values for three immersions data.

Treatment	Examination	Discoloration	Roughening	Local corrosion	Pitting	General corrosion	Total score	Percent of maximum total score
	Maximum score	3	4	9	12	12	40	100
Distilled Water	Before CPR	0	1	9	8	0	18	45
	After CPR	0	3	9	11	3	26	65
3% Sodium hydroxide	Before CPR	2	4	7	12	10	35	88
	After CPR	2	4	9	12	12	40	100
3% Sodium hydroxide + 0.168% sodium gluconate	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide + 0.24% ethylenediaminetetraacetic acid	Before CPR	1	4	7	12	7	31	78
	After CPR	3	4	8	12	12	39	98

Table 17. Macroscopic examination of the condition of the solutions after immersion of the cold rolled or hot rolled steel specimens. Mean values for three immersions data.

Treatment	Examination	Cloudiness	Precipitate	General appearance	Total score	Percent of maximum total score
	Maximum score	4	8	8	20	100
Distilled water		0	1	0	1	5
3% Sodium hydroxide		4	8	8	20	100
3% Sodium hydroxide + 0.168% sodium gluconate		4	8	8	20	100
3% Sodium hydroxide + 0.24% ethylenediamine-tetraacetic acid		4	8	8	20	100

Table 18. Over-all condition of the system expressed as a percentage of the maximum possible score for the sum of the solution and the specimens in the system before removal of corrosion products. Mean values for three immersions data.

Treatment	Combined score, percent AISI No. C 1008 steel		Interpretation of the combined scores using the method of Darrin (1946)	
	Cold rolled	Hot rolled	Designation	Degree of corrosion
Distilled water	32	32	Bad	Severe corrosion
3% Sodium hydroxide	93	92	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.168% sodium gluconate	100	100	Perfect	No indication
3% Sodium hydroxide + 0.24% ethylenediaminetetraacetic acid	90	85	Good	Definite, but probably satisfactory

get the same results using the prescribed experimental procedure. Corrosion test results for three different individuals following the same experimental procedure are reported in Table 19. The mean weight loss,

Table 19. Corrosion weight loss data obtained by three individuals using cold rolled AISI No. C 1008 steel specimens immersed in 3% sodium hydroxide plus 0.084% sodium gluconate for one week (7 days).

Immersions		Weight loss, mg/dm^2-week			
		Individuals			Immersion over-all means
		A	B	C	
I	Mean	4.08	4.03	4.48	4.19
	Standard deviation	0.61	0.29	0.29	
	Coefficient of variation, %	15.1	7.2	6.5	
II	Mean	4.68	3.90	3.95	4.18
	Standard deviation	0.59	0.41	0.17	
	Coefficient of variation,%	12.5	10.5	4.4	
Individual over-all means		4.38	3.96	4.21	4.18
Individual over-all standard deviation		0.640	0.333	0.356	
Individual over-all coefficient of variation, %		14.62	8.41	8.46	
Individual over-all mean error[1], %		±12.65	±7.28	±7.32	

[1] With confidence coefficient 0.95

standard deviation, coefficient of variation, and mean error are included in the table. An analysis of variance of the data is presented in Table 20. The F values indicated no significant difference between individuals

Table 20. Analysis of variance of corrosion weight loss data obtained by three individuals.

Source	Degrees of freedom	Sum of squares	Mean square	F
Total	23	5.23		
Immersions	1	0.002	0.002	0.01
Individuals	2	0.691	0.345	1.92
Interaction	2	1.30	0.649	3.60*
Error	18	3.24	0.180	

*Significant 5% level.

or immersions, but a significant interaction. The significant immersion-individual interaction is shown graphically in Figure 10.

The data were analyzed further, taking the data for each immersion separately. Table 21 gives the analyses of variance for each immersion. Again no significant difference between individuals was found. However, it is interesting to note that the sampling error mean square (error or within mean square) was the same for all three of the analyses.

Table 21. Analysis of variance of corrosion weight loss data obtained by three individuals.

Source	Degrees of freedom	Sum of squares	Mean square	F
Immersion 1				
Total	11	2.11		
Among	2	0.49	0.245	1.36
Within	9	1.62	0.180	
Immersion 2				
Total	11	3.12		
Among	2	1.50	0.750	4.17
Within	9	1.62	0.180	

Visual examination data for the specimens and liquids are not included, since the maximum possible score was reported by each individual throughout the test.

Studies on distilled water-sequestering agent systems

Results from a study conducted to determine the effects of certain sequestering agent, distilled water solutions on the corrosion of mild steel are reported in Table 22. Large differences in mean weight losses were found with the various sequestering agents. The mean weight loss decreased with each successive immersion of specimens in tetrasodium ethylenediaminetetraacetate solutions. Visual examination results for the steel specimens scored before and after corrosion products removal are reported in Table 23 and the visual examination scores of the solutions are reported in Table 24. Included in these tables are percent figures representing the total scores obtained with the specimens or solutions expressed as a percentage of their total possible score. The over-all condition of the systems is reported in Table 25. With the sodium gluconate solutions considerable corrosion was observed. The

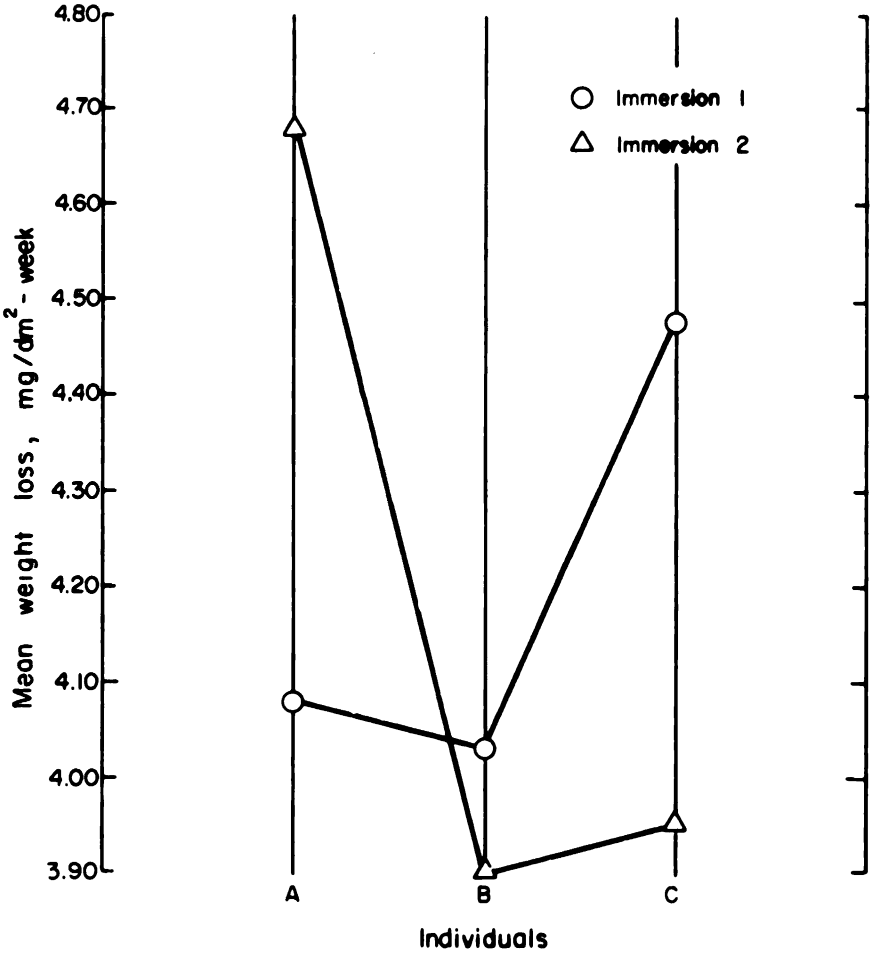

Fig. 10. Immersion-individual interaction obtained with steel specimens immersed in 3% sodium hydroxide plus 0.084% sodium gluconate.

Table 22. Corrosion weight loss results of cold rolled AISI No. C 1008 steel specimens immersed in distilled water, sequestering agent solutions for one week (7 days).

Agents	Mean weight loss, mg/dm^2-week					
	Immersions					Agent over-all means
	1	2	3	4	5	
Distilled water + 0.084% sodium gluconate	38.15	32.68	34.50	34.93	29.13	33.88
Distilled water + 0.156% tetrasodium ethylenediaminetetraacetate	167.38	161.03	150.93	146.60	132.73	151.73
Distilled water + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	2.70	3.23	3.30	3.70	3.45	3.28
Distilled water + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	3.18	3.00	3.03	3.70	3.00	3.18
Immersion over-all means	52.85	49.98	47.94	47.23	42.08	48.02

Table 23. Macroscopic examination of the corrosive effects of distilled water, sequestering agent solutions on cold rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatment	Examination	Discoloration	Roughening	Local corrosion	Pitting	General corrosion	Total score	Percent of maximum total score
	Maximum score	3	4	9	12	12	40	100
Distilled water	Before CPR	1	2	7	11	4	25	62
+ 0.084% sodium gluconate	After CPR	3	3	9	10	8	33	82
Distilled water	Before CPR	1	2	7	12	6	28	70
+ 0.156% tetrasodium ethylenediaminetetraacetate	After CPR	2	2	8	12	7	31	78
Distilled water	Before CPR	3	4	9	12	12	40	100
+ 0.057% trisodium phosphate (Na_3PO_4 $12H_2O$)	After CPR	3	4	9	12	12	40	100
Distilled water	Before CPR	3	4	8	12	12	39	98
+ 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7$ $10H_2O$)	After CPR	3	4	9	12	12	40	100

Table 24. Macroscopic examination of the condition of the solutions after immersion of cold rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatment	Examination	Cloudiness	Precipitate	General appearance	Total score	Percent of maximum total score
	Maximum score	4	8	8	20	100
Distilled water + 0.084% sodium gluconate		2	4	3	9	45
Distilled water + 0.156% tetrasodium ethylenediaminetetraacetate		1	2	3	6	30
Distilled water + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)		4	8	8	20	100
Distilled water + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)		4	8	8	20	100

Table 25. Over-all condition of the system expressed as a percentage of the maximum possible score for the sum of the solution and the specimens in the system before removal of the corrosion products. Mean values for five immersions data.

Treatment	Combined score, percent	Interpretation of the combined scores using the method of Darrin (1946)	
		Designation	Degree of corrosion
Distilled water + 0.084% sodium gluconate	57	Bad	Severe corrosion
Distilled water + 0.156% tetrasodium ethylenediaminetetraacetate	57	Bad	Severe corrosion
Distilled water + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	100	Perfect	No indication
Distilled water + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	98	Excellent	Minor, but very satisfactory

corrosion products were generally black or dark brown-to-yellowish in color, existing as a tightly adhering, slightly rough layer on the surface of the specimens. Some pitting and considerable general corrosion were visible before removal of the corrosion products. After their removal some of the general corrosion effects were still apparent and more pitting was visible. The over-all nature of the corrosion products was such that they were effectively removed by the corrosion products removal process after each immersion. Precipitation of corrosion products, solution cloudiness, and a generally poor solution appearance was observed. The over-all condition of the system (specimens and solutions) was assessed and interpreted according to Darrin's (1946) methods as bad, with severe corrosion. Considerable corrosion was also apparent with the tetrasodium ethylenediaminetetraacetate solutions. The corrosion products were a dark red-to-brown color, and existed as a thin, slightly rough layer on the specimen surface before corrosion products removal. The nature of these corrosion products were such that they were particularly difficult to remove. They seemed to become increasingly more difficult to remove after each successive immersion. Some of the corrosion products could not be removed and the amount increased with successive immersions. Considerable precipitation of corrosion products was observed, along with considerable solution cloudiness and a poor solution general appearance. The over-all condition of the system was assessed and interpreted according to Darrin's (1946) methods as bad, with severe corrosion. The phosphate solutions showed no visible corrosion effects.

Studies on distilled water-sodium hydroxide-sequestering agent systems

Sequestering agent effects

The results of a test conducted to determine the effects of four water softening agents on the corrosion of mild steel in 3% sodium hydroxide solutions are presented in Table 26. In comparing the effects of these four agents one to the other and to the 3% sodium hydroxide control, the "use concentrations" (that concentration of agent required to soften water of 12 grains per gallon total hardness as $CaCO_3$) are used. Three concentrations of sodium gluconate (A_I) and tetrasodium ethylenediaminetetraacetate (A_{II}) and one concentration of trisodium phosphate (A_{III}) and tetrasodium pyrophosphate (A_{IV}) were tested. The use concen-

Table 26. Corrosion weight loss results of cold rolled AISI No. C 1008 steel specimens immersed for one week (7 days) in alkaline detergent, distilled water solutions.

Agents	Mean weight loss, mg/dm^2-week					
	Immersions					Agent over-all means
	1	2	3	4	5	
3% Sodium hydroxide	2.90	2.50	3.15	1.95	3.23	2.74
3% Sodium hydroxide + 0.042% sodium gluconate	4.68	3.03	3.05	2.75	2.40	3.18
3% Sodium hydroxide + 0.084% sodium gluconate	4.03	3.90	2.65	2.78	3.03	3.28
3% Sodium hydroxide + 0.168% sodium gluconate	4.55	3.38	3.43	3.73	2.45	3.51
3% Sodium hydroxide +0.078% tetrasodium ethylenediaminetetraacetate	6.03	2.83	1.83	2.88	2.08	3.13
3% Sodium hydroxide +0.156% tetrasodium ethylenediaminetetraacetate	5.98	3.53	1.95	2.33	3.38	3.43
3% Sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate	5.63	3.93	2.35	2.35	3.58	3.57
3% Sodium hydroxide + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	2.85	2.93	2.20	2.23	3.80	3.00
3% Sodium hydroxide + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	3.13	2.33	2.90	2.55	3.78	3.14
Immersion over-all means	4.42	3.15	2.61	2.61	3.30	3.22

trations are 0.084% with A_I, 0.156% with A_{II}, and the concentration tested with A_{III} and A_{IV}. The results are presented in a manner that allows not only comparisons of agent effects, but also comparisons of specific agent effects to other agents at more than one concentration, and still further comparisons of the effects of A_I and A_{II} concentration on corrosion. The specific effects of concentration of A_I and A_{II} on corrosion are analyzed, and discussed in detail in the last section of this dissertation for direct comparison of these effects in distilled water and hard water. An analysis of variance of the weight loss data (Table 26) for the steel specimens immersed in the alkaline detergent solutions is given in Table 27. The analysis shows that the agent, immersion, and interaction effects are each highly significant. The agent and immersion over-all means are ranked from smallest to largest values and tested for significance by Harter's (1960) critical values for Duncan's new multiple range test in Figures 11 and 12. A horizontal line connects means which are not significantly different. Codes were used to facilitate the presentation of these results. The immersion-agent interaction is shown graphically in Figure 13.

Table 27. Analysis of variance of corrosion weight loss data for steel specimens immersed in alkaline detergent, distilled water solutions.

Source	Degrees of freedom	Sum of squares	Mean square	F
Total	179	216.93		
Immersions	4	78.55	19.64	100.72**
Agents	8	10.79	1.35	6.92**
Interaction	32	101.23	3.16	16.20**
Error	135	26.36	0.195	

**Significant, 1% level.

The results of a number of statistical tests on the data to assess some of its general characteristics follow.

Individual replicate weight loss values ranked by immersions for 3% sodium hydroxide and 3% sodium hydroxide plus 0.156% tetrasodium ethylenediaminetetraacetate did not show a significant concordance (Walker and Lev (1953)). This indicates that the rank of a given replicate from immersion to immersion is independent of its rank in a previous immersion.

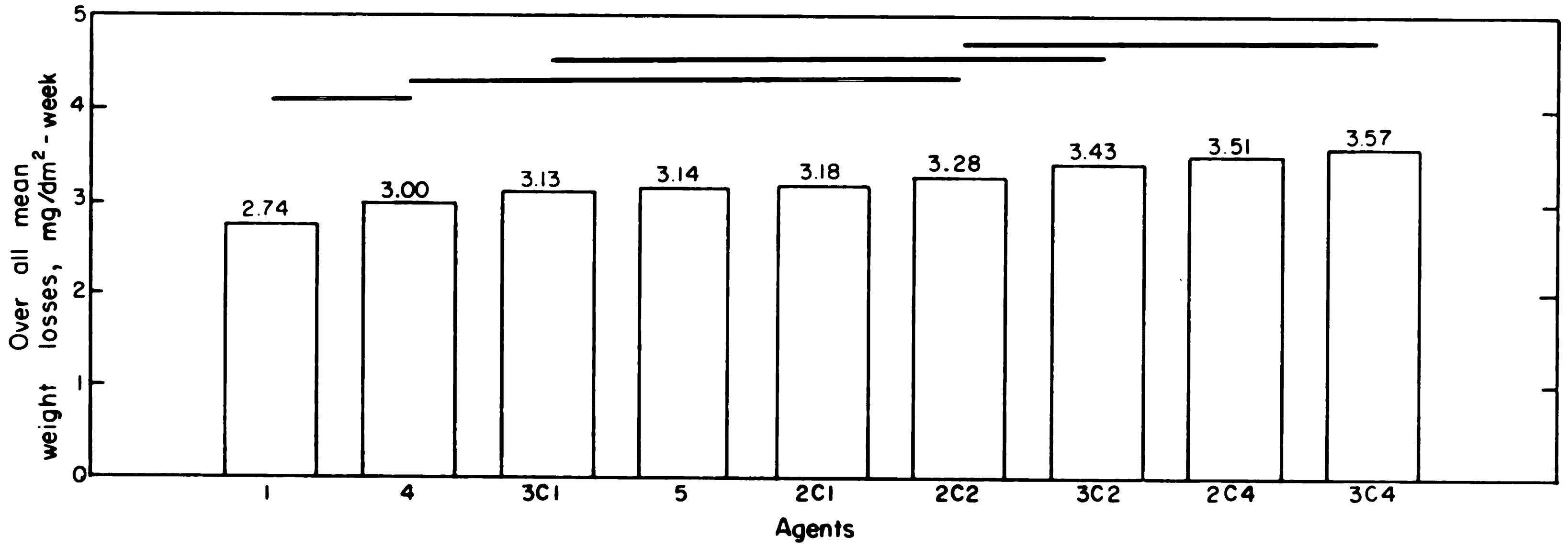

Fig. 11. Comparison of the amount of corrosion of steel specimens immersed in alkaline sequestering agent solutions made with distilled water: (1, 3% Sodium hydroxide; 2C1, 3% Sodium hydroxide + 0.042% sodium gluconate; 2C2, 3% Sodium hydroxide + 0.084% sodium gluconate; 2C4, 3% Sodium hydroxide + 0.168% sodium gluconate; 3C1, 3% Sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate; 3C2, 3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate; 3C4, 3% Sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate; 4, 3% Sodium hydroxide + 0.057% trisodium phosphate·12 water; 5, 3% Sodium hydroxide + 0.293% tetrasodium pyrophosphate·10 water).

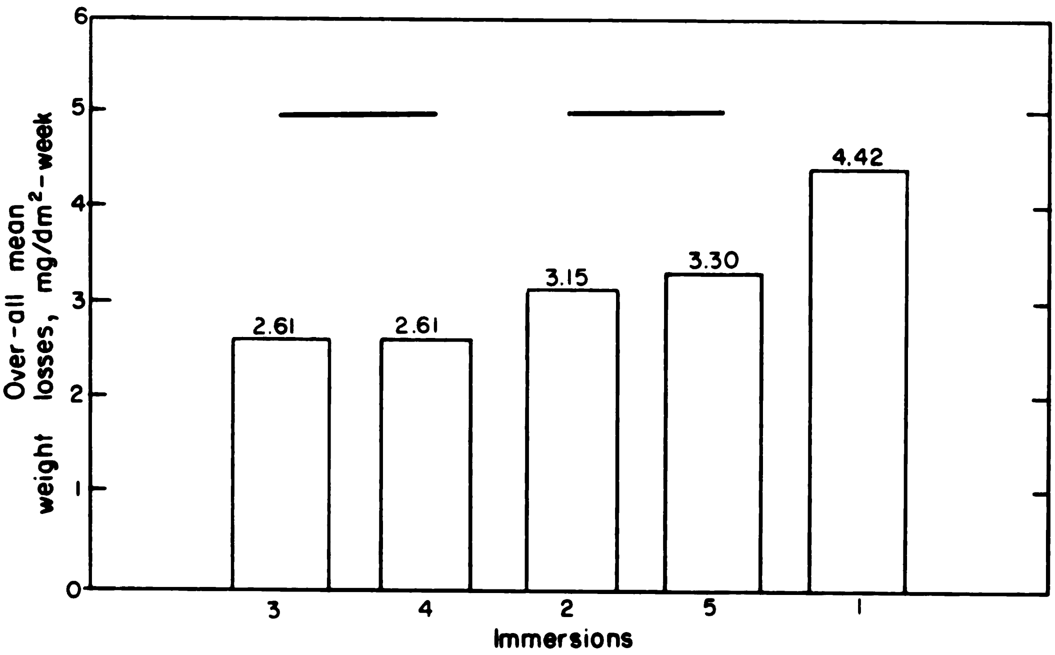

Fig. 12. Comparison of the amount of corrosion obtained with different immersions of steel specimens in alkaline sequestering agent solutions made with distilled water.

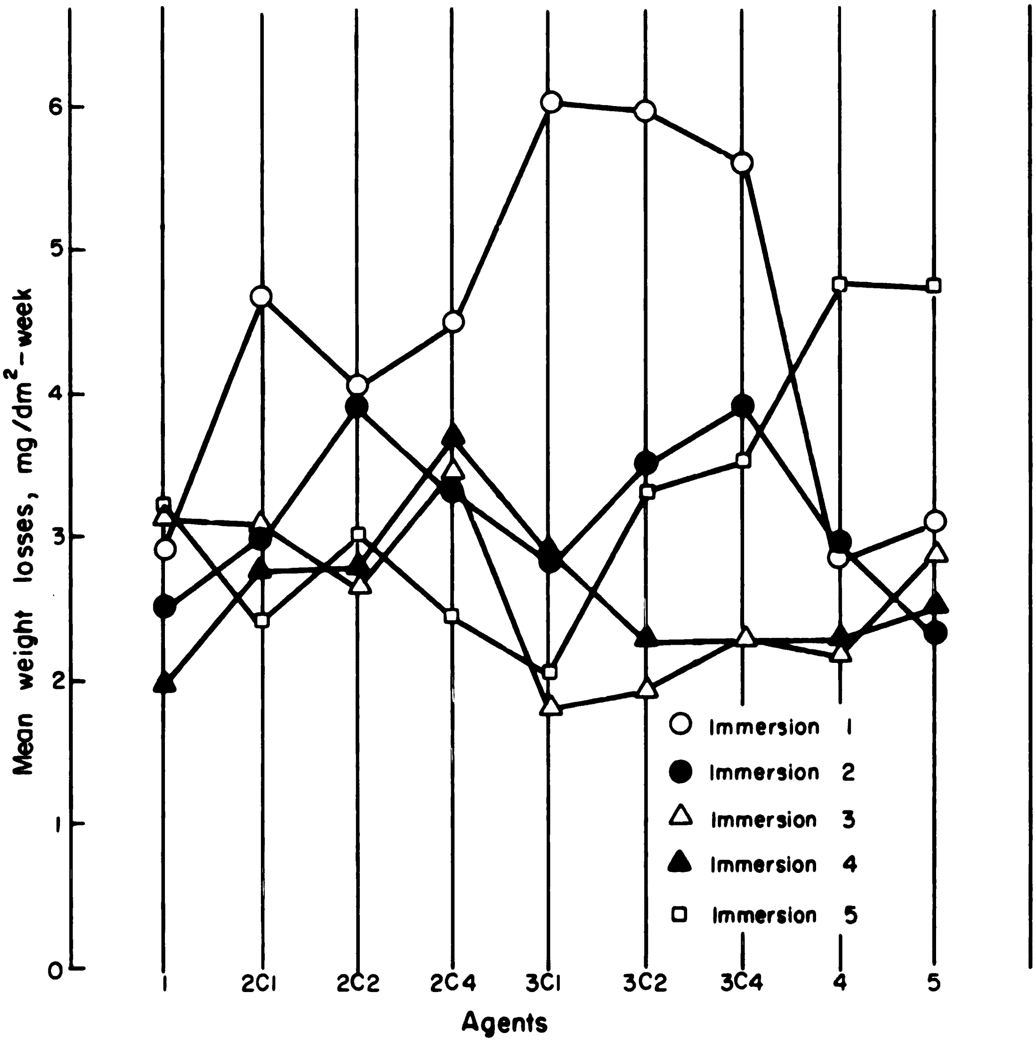

Fig. 13. Immersion-agent interaction.

The corrosion weight loss results obtained with 3% sodium hydroxide and 3% sodium hydroxide plus 0.156% tetrasodium ethylenediaminetetraacetate solutions from immersion-to-immersion were tested for dependence between immersions. Linear correlation coefficients were calculated and tested for significance at the 5% probability level, for each possible combination of immersions. There were ten combinations for each agent. The correlation coefficients were not significant, indicating that the results from any particular immersion are not dependent upon the results of some other immersion. The same results were found for correlations of weight loss results of immersion one against immersion two for 3% sodium hydroxide solutions of: 0.084% sodium gluconate, 0.057% trisodium phosphate, and 0.293% tetrasodium pyrophosphate. The linear correlation coefficients were not significantly different from zero, indicating that the outcome of a subsequent immersion is independent (or not significantly affected by) of a previous immersion's effects.

The data for five of the previously mentioned agents each showed a highly significant concordance when the immersions were ranked by the replicates. This shows that when a given immersion is either more or less corrosive than another immersion its effect is obtained over all replicates.

The experimental design as shown in Figure 6 was set up so that the corrosion weight loss data for the 10 agents (distilled water plus the nine alkaline solutions) could be analyzed together by analysis of variance. However, Cochran's Test for homogeneity of variances (Dixon and Massey (1957)) showed that the variances were not equal (homogeneous) at the 1% significance level. The variance for the distilled water data was much larger than the variances for the alkaline solutions' data. Cochran's Test showed homogeneity of variance for the alkaline solutions' data. Since homogeneity of variance which is essential to analysis of variance was found for the alkaline solutions, they were analyzed together.

To answer the question as to whether the agents as analyzed (five different agents and three concentrations of two of these, to give the total of nine agents) would give the same results if broken down into a five agent analysis and analyses comparing the three concentrations (of each of the two agents) directly, it was found that the answer lies in the fact that a common variance exists for the nine agents (homogeneity was found). The results of such an analysis of variance and tests of significance of the ranked agent over-all means (not presented) for these five agents (the upper and lower concentrations of sodium gluconate and tetrasodium ethylenediaminetetraacetate were not included in this analysis) showed the same significant differences for these five agents as was found in the nine agent analysis shown in Figure 11. Individual analyses of the two agents at three concentrations showed the same significant differences for the three concentrations of each agent as was found in the nine agent analysis shown in Figure 11.

Visual examination results for the steel specimens scored according to Darrin's system before and after corrosion products removal are shown in Table 28. The visual examination scores of the solutions are shown in Table 29. Included in these tables are the total scores of the four replicate specimens or solutions as percentages of the total score possible. In addition, Table 30 presents the over-all condition of the system as a percentage of the maximum possible score.

The 3% sodium hydroxide control showed some discoloration, local and general corrosion before corrosion products removal. After corrosion products removal the effects of a small amount of local corrosion was apparent. The A_I, A_{III}, and A_{IV} solutions showed no visible corrosion damage to the specimens or contamination of the solutions. The appearance of the specimens after immersion in these solutions seemed improved rather than harmed. With A_{II} the specimens showed discoloration (dark red-to-brown color), local corrosion and considerable general corrosion before removal of the corrosion products. Some of the discoloration, local and general corrosion effects were still apparent after removal of the corrosion products.

A comparison was made between distilled water solutions of 3% sodium hydroxide, 3% sodium hydroxide plus 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$), 3% sodium hydroxide plus 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$) (data in Table 26) and distilled water solutions of 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$) and 2.93% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$) (data in Table 22). The analysis of variance

Table 28. Macroscopic examination of the corrosion effects of alkaline detergent, distilled water solutions on cold rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatment	Examination	Discoloration	Roughening	Local corrosion	Pitting	General corrosion	Total score	Percent of maximum total score
	Maximum score	3	4	9	12	12	40	100
3% Sodium hydroxide	Before CPR	2	4	7	12	10	35	88
	After CPR	3	4	8	12	12	39	98
3% Sodium hydroxide + 0.042% sodium gluconate	Before CPR	3	4	8	12	11	38	95
	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide + 0.084% sodium gluconate	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide + 0.168% sodium gluconate	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate	Before CPR	1	4	7	12	7	31	78
	After CPR	2	4	8	12	11	37	92
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate	Before CPR	1	4	7	12	6	30	75
	After CPR	2	4	8	12	11	37	92
3% Sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate	Before CPR	1	4	7	12	6	30	75
	After CPR	2	4	8	12	11	37	92
3% Sodium hydroxide + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	Befroe CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100

Table 29. Macroscopic examination of the condition of the alkaline detergent, distilled water solutions after immersion of cold rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatment	Examination	Cloudiness	Precipitate	General appearance	Total score	Percent of maximum total score
	Maximum score	4	8	8	20	100
3% Sodium hydroxide		4	8	8	20	100
3% Sodium hydroxide + 0.042% sodium gluconate		4	8	8	20	100
3% Sodium hydroxide + 0.084% sodium gluconate		4	8	8	20	100
3% Sodium hydroxide + 0.168% sodium gluconate		4	8	8	20	100
3% Sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate		4	8	8	20	100
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate		4	8	8	20	100
3% Sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate		4	8	8	20	100
3% Sodium hydroxide + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)		4	7	7	18	90
3 % Sodium hydroxide + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)		4	8	8	20	100

Table 30. Over-all condition of the system expressed as a percentage of the maximum possible score for the sum of the solution and the specimens in the system before removal of the corrosion products. Mean values for five immersions data.

Treatment	Combined score, percent	Interpretation of the combined scores using the method of Darrin (1946)	
		Designation	Degree of corrosion
3% Sodium hydroxide	92	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.042% sodium gluconate	97	Excellent	Minor, but very satisfactory
3% Sodium hydroxide + 0.084% sodium gluconate	100	Perfect	No indication
3% Sodium hydroxide + 0.168% sodium gluconate	100	Perfect	No Indication
3% Sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate	85	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetatraacetate	83	Fair	Questionable
3% Sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate	83	Fair	Questionable
3% Sodium hydroxide + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	97	Excellent	Minor, but very satisfactory
3% Sodium hydroxide + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	100	Perfect	No indication

results of the corrosion weight loss data for these solutions are given in Table 31. The agent and immersion over-all means are ranked and tested

Table 31. Analysis of variance of corrosion weight loss data for steel specimens immersed in distilled water and 3% sodium hydroxide,phosphate solutions.

Source	Degrees of freedom	Sum of squares	Mean square	F
Total	99	53.79		
Immersions	4	15.65	3.91	31.28**
Agents	4	3.37	0.832	6.74**
Interaction	16	25.42	1.59	12.72**
Error	75	9.35	0.125	

**Significant, 1% level.

for significance in Table 32.

Table 32. Comparison of agent and immersion over-all mean weight losses.

Agents	Agent over-all means, mg/dm^2-week	Immersions	Immersion over-all means, mg/dm^2-week
Distilled water + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	3.28	5	3.85
		1	2.95
Distilled water + 0.293% tetrasodium pyrophosphate ($N_4P_2O_7 \cdot 10H_2O$)	3.18	3	2.92
		4	2.83
3% Sodium hydroxide + 0.293% tetrasodium pyrophosphate ($N_4P_2O_7 \cdot 10H_2O$)	3.14	2	2.80
3% Sodium hydroxide + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	3.00		
3% Sodium hydroxide	2.74		

The results show that the distilled water plus phosphate solutions used tend to be more corrosive than the 3% sodium hydroxide plus phosphate solutions, which are in turn more corrosive than the 3% sodium hydroxide control. The distilled water plus phosphate solutions were effective inhibitors in light of the concentrations used. These results indicate that the corrosion rate in the rinse sections of bottle washers could be reduced to a value near that found in the alkaline wash sections through incorporation of such agents.

Temperature effects

The corrosion weight loss results for the study conducted to determine the influence of temperature on alkaline detergent, distilled water solution corrosivity are presented in Table 33. The 150°F data is taken from Tables 26, 28, 29, and 30. Analysis of variance results for each of the agents tested are reported in Table 34. Temperature, immersion and interaction effects were highly significant in each case. The over-all means are ranked and tested for significant differences in Table 35.

Table 33. Corrosion weight loss results of cold rolled AISI No. C 1008 steel specimens immersed in alkaline detergent, distilled water solutions at different temperatures for one week (7 days).

Treatments	Mean weight loss, mg/dm^2-week					
	Immersions					Temperature over-all means
	1	2	3	4	5	
3% Sodium hydroxide						
130°F	2.20	2.40	2.73	3.88	2.78	2.80
150°F	2.90	2.50	3.15	1.95	3.23	2.75
170°F	3.33	3.18	3.80	3.13	4.03	3.49
Immersion over-all means	2.81	2.69	3.23	2.98	3.34	3.01
3% Sodium hydroxide + 0.084% sodium gluconate						
130°F	4.10	3.90	2.78	4.20	3.83	3.76
150°F	4.03	3.90	2.65	2.78	3.03	3.28
170°F	4.63	4.33	4.78	4.78	6.58	5.02
Immersion over-all means	4.25	4.04	3.40	3.92	4.48	4.02
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate						
130°F	2.30	1.63	3.90	3.98	3.25	3.01
150°F	5.98	3.53	1.95	2.33	3.38	3.43
170°F	4.25	2.85	3.68	3.03	4.55	3.67
Immersion over-all means	4.18	2.67	3.18	3.11	3.73	3.37

Visual examination results for the specimens and solutions are presented in Tables 36, 37, and 38.

Table 34. Analysis of variance of corrosion weight loss data for steel specimens immersed in alkaline detergent, distilled water solutions at different temperatures.

Source	Degrees of freedom	Sum of squares	Mean square	F
3% Sodium hydroxide				
Total	59	31.01		
Immersions	4	3.58	0.895	3.89**
Temperature	2	6.93	3.47	15.10**
Interaction	8	10.16	1.27	5.53**
Error	45	10.34	0.230	
3% Sodium hydroxide + 0.084% sodium gluconate				
Total	59	68.34		
Immersions	4	7.86	1.965	7.68**
Temperature	2	32.25	16.125	62.99**
Interaction	8	16.69	2.086	8.15**
Error	45	11.54	0.256	
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate				
Total	59	79.59		
Immersions	4	16.51	4.128	18.76**
Temperatures	2	4.47	2.235	10.16**
Interaction	8	48.70	6.088	27.67**
Error	45	9.91	0.220	

** Significant, 1% level.

Table 35. Comparison of the amount of corrosion of steel specimens immersed in alkaline detergent, distilled water solutions at different temperatures.

Agents	Temperatures, °F	Temperature over-all means, mg/dm^2-week	Immersions	Immersion over-all means, mg/dm^2-week
3% Sodium hydroxide	170	3.49	5	3.34
	130	2.80	3	3.23
	150	2.75	4	2.98
			1	2.81
			2	2.69
3% Sodium hydroxide + 0.084% sodium gluconate	170	5.02	5	4.48
	130	3.76	1	4.25
	150	3.28	2	4.04
			4	3.92
			3	3.40
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate	170	3.67	1	4.18
	150	3.43	5	3.73
	130	3.01	3	3.18
			4	3.11
			2	2.67

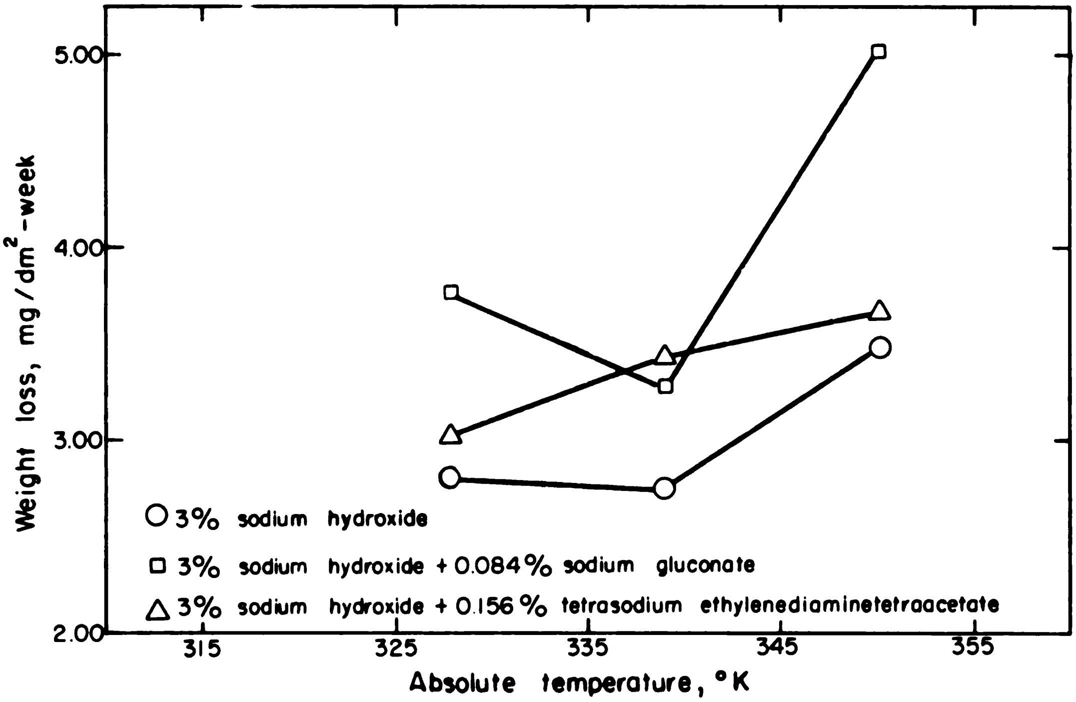

Fig. 14. Corrosion weight loss of steel specimens immersed in alkaline detergent, distilled water solutions at different temperatures for one week (7 days). Temperature over-all mean weight losses plotted.

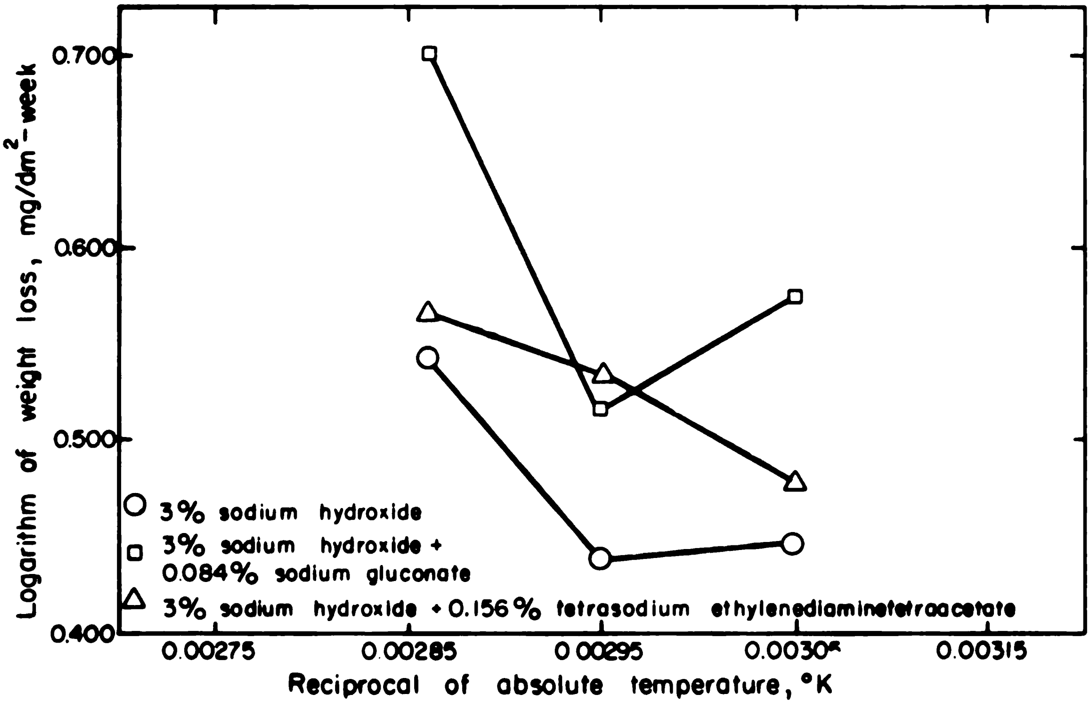

Fig. 15. Arrhenius plots of corrosion weight loss of steel specimens immersed in alkaline detergent, distilled water solutions at different temperatures for one week (7 days). Temperature over-all mean weight losses plotted.

Table 36. Macroscopic examination of the corrosion effects of alkaline detergent, distilled water solutions at different temperatures on cold rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatments	Examination	Discoloration	Roughening	Local corrosion	Pitting	General corrosion	Total score	Percent of maximum total score
	Maximum score	3	4	9	12	12	40	100
3% Sodium hydroxide								
130°F	Before CPR	3	4	9	12	11	39	98
	After CPR	3	4	9	12	11	39	98
150°F	Before CPR	2	4	7	12	10	35	88
	After CPR	3	4	8	12	12	39	98
170°F	Before CPR	2	4	7	12	10	35	88
	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide + 0.084% sodium gluconate								
130°F	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
150°F	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
170°F	Before CPR	2	4	7	12	11	36	90
	After CPR	3	4	9	12	11	39	98
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate								
130°F	Before CPR	2	4	7	12	12	37	92
	After CPR	2	4	9	12	11	38	95
150°F	Before CPR	1	4	8	12	6	31	78
	After CPR	2	4	8	12	11	37	92
170°F	Before CPR	2	4	8	12	10	36	90
	After CPR	3	4	8	12	12	39	98

Table 37. Macroscopic examination of the condition of the solutions used at different temperatures after immersion of cold rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatments	Examination	Cloudiness	Precipitate	General appearance	Total score	Percent of maximum total score
	Maximum score	4	8	8	20	100
3% Sodium hydroxide						
130°F		4	8	8	20	100
150°F		4	8	8	20	100
170°F		4	8	8	20	100
3% Sodium hydroxide + 0.084% sodium gluconate						
130°F		4	8	8	20	100
150°F		4	8	8	20	100
170°F		3	7	7	17	85
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate						
130°F		4	8	8	20	100
150°F		4	8	8	20	100
170°F		3	7	7	17	85

Table 38. Over-all conditions of the systems at different temperatures expressed as a percentage of the maximum possible score for the sum of the solution and the specimens in the system before removal of corrosion products. Mean values for five immersions data.

Treatment	Combined score, percent	Interpretation of the combined scores using the method of Darrin (1946)	
		Designation	Degree of corrosion
3% Sodium hydroxide			
130°F	98	Excellent	Minor, but very satisfactory
150°F	92	Good	Definite, but probably satisfactory
170°F	92	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.084% sodium gluconate			
130°F	100	Perfect	No indication
150°F	100	Perfect	No indication
170°F	88	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate			
130°F	95	Excellent	Minor, but very satisfactory
150°F	85	Good	Definite, but probably satisfactory
170°F	88	Good	Definite, but probably satisfactory

Surface-active agent effects

Wetting agents are sometimes added to alkaline sequestering agent solutions to further improve their detergency. One such surface-active agent is Triton QS-15. It is an amphoteric surface-active agent, of the oxyethylated sodium salt type, containing both anionic and cationic centers. A test was conducted to determine the corrosive effect of this wetting agent in combination with sodium hydroxide and sodium gluconate. The corrosion weight loss results of this test are presented in Table 39.

Table 39. Corrosion weight loss results for cold rolled AISI No. C 1008 steel specimens immersed in an alkaline sequestering agent solution with and without a wetting agent for one week (7 days). Solutions prepared with distilled water.

Agents	Mean weight loss, mg/dm^2-week		
	Immersions		Agent over-all means
	1	2	
3% Sodium hydroxide + 0.084% sodium gluconate	4.08	4.68	4.38
3% Sodium hydroxide + 0.084% sodium gluconate + 0.015% Triton QS-15	4.65	4.58	4.61
Immersion over-all means	4.36	4.63	4.49

Table 40 gives the analysis of variance results for this test which show no significant difference between the two solutions (one with and one without the wetting agent) or between the two immersions in corrosivity. Visual examination data for this study (not presented) showed no evidence

Table 40. Analysis of variance of corrosion weight loss data for steel specimens immersed in an alkaline sequestering agent solution with and without a wetting agent.

Source	Degrees of freedom	Sum of square	Mean square	F
Total	15	4.29		
Immersions	1	0.276	0.276	0.99
Agents	1	0.226	0.226	0.81
Interaction	1	0.456	0.456	1.64
Error	12	3.33	0.278	

of corrosion with either solution. The maximum possible score for the specimens and solutions was found throughout the study.

Length of immersion effect

Results of a study conducted to determine the variation in amount of corrosion as affected by the length of immersion are presented in Tables 41, 42, 43, 44, 45, and 46. Analyses of variance results, presented in Table 42, show that only with 3% sodium hydroxide plus 0.156% tetrasodium ethylenediaminetetraacetate in the first immersion, was there a significant difference between the amounts of corrosion found with 1, 3, 5, or 7 days of immersion. (It should be noted that separate sets of specimens were employed in each immersion period.) Presented in Table 43 is a comparison of the mean weight losses for each agent and immersion. With 3% sodium hydroxide plus 0.156% tetrasodium ethylenediaminetetraacetate, significantly more corrosion was found with the 7 day immersion than with the 1, 3, and 5 day immersions which were themselves not significantly different. The visual examination results indicated a poorer over-all condition with the 7 day immersion period for both 3% sodium hydroxide and 3% sodium hydroxide plus 0.156% tetrasodium ethylenediaminetetraacetate and a poorer over-all condition with the 5 day immersion period for 3% sodium hydroxide plus 0.084% sodium gluconate.

Studies on hard water-sodium hydroxide-sequestering agent systems

Corrosion weight loss results from a study conducted to assess the effects of four water softening agents on the corrosion of mild steel in 3% sodium hydroxide solutions are presented in Table 47. Hard water of 12 grains per gallon total hardness as calcium carbonate was used in preparing the solutions. As in the distilled water-sodium hydroxide-sequestering agent system studies three concentrations of sodium gluconate (A_I) and tetrasodium ethylenediaminetetraacetate (A_{II}) and one concentration of trisodium phosphate (A_{III}) and tetrasodium pyrophosphate (A_{IV}) were used. In comparing agent effects the use concentrations are used. For A_I this is the 0.084% level (22C2) and for A_{II} this is the 0.156% level (33C2) and these are compared to the control (3% sodium hydroxide (11)) and to the use concentrations of A_{III} (44) and A_{IV} (55). (The numbers given in parentheses are codes for the various agents and concentrations of agents tested, which are used in Figure 16 to facilitate the

Table 41. Corrosion of cold rolled AISI No. C 1008 steel specimens immersed for increasing lengths of time in alkaline detergent, distilled water solutions.

Agents	Mean weight loss, mg/dm^2									
	Immersion 1				Agent over-all means	Immersion 2				Agent over-all means
	Length of immersion, days					Length of immersion, days				
	1	3	5	7		1	3	5	7	
3% Sodium hydroxide	3.40	3.18	2.68	2.90	3.04	2.45	2.55	3.90	2.50	2.85
3% Sodium hydroxide + 0.084% sodium gluconate	4.35	5.05	5.00	4.03	4.61	3.28	3.82	4.38	3.90	3.84
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate	2.62	2.72	3.50	5.98	3.70	2.82	3.02	3.58	3.53	3.24

Table 42. Analysis of variance of corrosion weight loss data for steel specimens immersed for increasing lengths of time in alkaline detergent, distilled water solutions.

Source	Immersions							
	1				2			
	Degrees of freedom	Sum of squares	Mean square	F	Degrees of freedom	Sum of squares	Mean square	F
3% Sodium hydroxide								
Total	15	3.54			15	15.42		
Between	3	1.21	0.403	2.08	3	5.90	1.97	2.48
Within	12	2.33	0.194		12	9.52	0.793	
3% Sodium hydroxide + 0.084% sodium gluconate								
Total	15	6.99			15	14.78		
Between	3	3.02	1.01	3.05	3	2.44	0.813	0.791
Within	12	3.97	0.331		12	12.34	1.03	
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate								
Total	15	35.01			15	5.40		
Between	3	29.29	9.76	20.47**	3	1.65	0.550	1.76
Within	12	5.72	0.477		12	3.75	0.313	

**Significant, 1% level.

Table 43. Comparison of the amount of corrosion of steel specimens immersed for increasing lengths of time in alkaline detergent, distilled water solutions.

Agents	Immersions			
	1		2	
	Length of immersion, days	Mean weight, loss mg/dm^2	Length of immersion, days	Mean weight loss, mg/dm^2
3% Sodium hydroxide	1	3.40	5	3.90
	3	3.18	3	2.55
	7	2.90	7	2.50
	5	2.68	1	2.45
3% Sodium hydroxide + 0.084% sodium gluconate	3	5.05	5	4.38
	5	5.00	7	3.90
	1	4.35	3	3.82
	7	4.03	1	3.28
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate	7	5.98	5	3.58
	5	3.50	7	3.53
	3	2.72	3	3.02
	1	2.62	1	2.82

Table 44. Macroscopic examination of cold rolled AISI No. C 1008 steel specimens immersed for different lengths of time in alkaline detergent, distilled water solutions. Mean values for two immersions data.

Treatments	Examination	Discoloration	Roughening	Local corrosion	Pitting	General corrosion	Total score	Percent of maximum total score
	Maximum score	3	4	9	12	12	40	100
3% Sodium hydroxide								
1 day	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
3 days	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
5 days	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
7 days	Before CPR	2	4	9	12	9	36	90
	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide + 0.084% sodium gluconate								
1 day	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
3 days	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100
5 days	Before CPR	0	4	9	12	3	28	70
	After CPR	3	4	9	12	12	40	100
7 days	Before CPR	3	4	9	12	12	40	100
	After CPR	3	4	9	12	12	40	100

Table 44. Continued.

Treatments	Examination	Discoloration	Roughening	Local corrosion	Pitting	General corrosion	Total score	Percent of maximum total score
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate								
1 day	Before CPR	2	4	6	12	12	36	90
	After CPR	2	4	8	12	10	36	90
3 days	Before CPR	2	3	6	12	12	35	88
	After CPR	3	4	9	12	12	40	100
5 days	Before CPR	2	4	6	12	12	36	90
	AfterCPR	3	4	9	12	12	40	100
7 days	Before CPR	0	4	6	12	4	26	65
	After CPR	3	4	9	12	12	40	100

Table 45. Macroscopic examination of the condition of the solutions used for the different lengths of immersion of cold rolled AISI No. C 1008 steel specimens. Mean values for two immersions data.

Treatments	Examination	Cloudiness	Precipitate	General appearance	Total score	Percent of maximum total score
	Maximum score	4	8	8	20	100
3% Sodium hydroxide						
1 day		4	8	8	20	100
3 days		4	8	8	20	100
5 days		4	8	8	20	100
7 days		4	8	8	20	100
3% Sodium hydroxide + 0.084% sodium gluconate						
1 day		4	8	8	20	100
3 days		4	8	8	20	100
5 days		4	8	8	20	100
7 days		4	8	8	20	100
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate						
1 day		4	8	8	20	100
3 days		4	8	8	20	100
5 days		4	8	8	20	100
7 days		4	8	8	20	100

Table 46. Over-all condition of the systems tested for different lengths of time expressed as a percentage of the maximum possible score for the sum of the solution and the specimens in the systems before removal of corrosion products. Mean values for two immersions data.

Treatment	Combined score, percent	Interpretation of the combined scores using the method of Darrin (1946)	
		Designation	Degree of corrosion
3% Sodium hydroxide			
1 day	100	Perfect	No indication
3 days	100	Perfect	No indication
5 days	100	Perfect	No indication
7 days	93	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.084% sodium gluconate			
1 day	100	Perfect	No indication
3 days	100	Perfect	No indication
5 days	80	Fair	Questionable
7 days	100	Perfect	No indication
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate			
1 day	93	Good	Definite, but probably satisfactory
3 days	92	Good	Definite, but probably satisfactory
5 days	93	Good	Definite, but probably satisfactory
7 days	77	Fair	Questionable

Table 47. Corrosion weight loss results of cold rolled AISI No. C 1008 steel specimens immersed for one week (7 days) in alkaline detergent, hard water solutions of 12 grains per gallon total hardness as calcium carbonate.

Agents	Mean weight loss, mg/dm^2-week					
	Immersions					Agent over-all means
	1	2	3	4	5	
3% Sodium hydroxide	3.50	3.35	4.00	3.83	5.95	4.13
3% Sodium hydroxide + 0.042% sodium gluconate	8.03	8.78	9.03	7.85	9.18	8.57
3% Sodium hydroxide + 0.084% sodium gluconate	7.13	6.85	8.05	6.55	7.48	7.21
3% Sodium hydroxide + 0.168% sodium gluconate	5.80	5.60	8.35	6.38	7.03	6.63
3% Sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate	3.35	3.10	3.38	2.05	3.85	3.15
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate	3.55	3.43	3.60	2.03	4.03	3.33
3% Sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate	3.18	2.48	4.13	1.93	3.35	3.01
3% Sodium hydroxide + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	2.93	2.60	2.38	3.13	5.23	3.25
3% Sodium hydroxide + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	3.25	2.65	2.15	4.70	4.70	3.49
Immersion over-all means	4.52	4.31	5.01	4.27	5.64	4.75

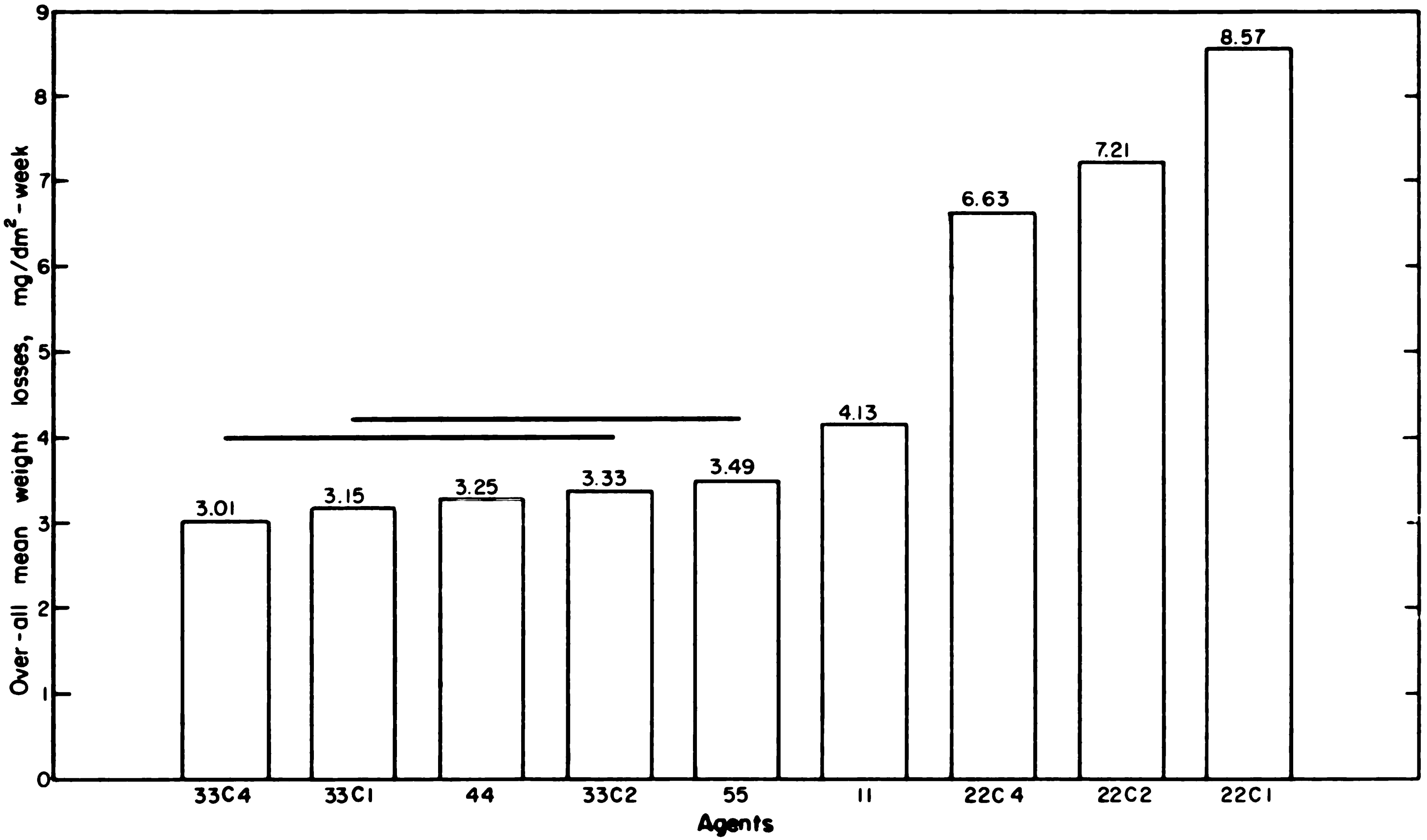

Fig. 16. Comparison of the amount of corrosion of steel specimens immersed in alkaline sequestering agent solutions made with hard water: (11, 3% Sodium hydroxide; 22C1, 3% Sodium hydroxide + 0.042% sodium gluconate; 22C2, 3% Sodium hydroxide + 0.084% sodium gluconate; 22C4, 3% Sodium hydroxide + 0.168% sodium gluconate; 33C1, 3% Sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate; 33C2, 3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate; 33C4, 3% Sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate; 44, 3% Sodium hydroxide + 0.057% trisodium phosphate·12 water; 55, 3% Sodium hydroxide + 0.293% tetrasodium pyrophosphate·10 water).

presentation of the results.) An analysis of variance of the weight loss data (Table 47) for the steel specimens immersed in the alkaline detergent solutions is given in Table 48. The analysis shows that the agent, immersion, and interaction effects are each highly significant. The agent and immersion over-all means are ranked and tested for significant differences in Figures 16 and 17 respectively. The results are presented in a manner that allows not only comparisons of agent effects, but also comparisons of specific agent effects to other agents at more than one concentration, and still further comparisons of the effects of A_I and A_{II} concentration on corrosion. The specific effects of concentration of A_I and A_{II} on corrosion are analyzed, and discussed in detail in the last section of this dissertation in order to allow direct comparison of these effects in distilled water and hard water.

Table 48. Analysis of variance of corrosion weight loss data for steel specimens immersed in alkaline detergent, hard water solutions.

Source	Degrees of freedom	Sum of squares	Mean square	F
Total	179	887.87		
Immersions	4	47.96	11.99	33.87**
Agents	8	720.78	90.10	254.52**
Interaction	32	71.29	2.23	6.30**
Error	135	47.84	0.354	

**Significant, 1% level

Visual examination results for the steel specimens scored according to Darrin's (1946) system before and after corrosion products removal are shown in Table 49. The visual examination scores of the solutions are given in Table 50. Included in these tables are percent figures representing the total scores of the four replicate specimens or solutions expressed as a percentage of the total possible. In addition, Table 51 presents the over-all condition of the system, sum of the liquid and the specimens in the system before removal of corrosion products, as a percentage of the maximum possible score. The 3% sodium hydroxide control showed considerable discoloration and general corrosion before corrosion products removal. After their removal less discoloration and general corrosion was observed and the effects of some local corrosion became

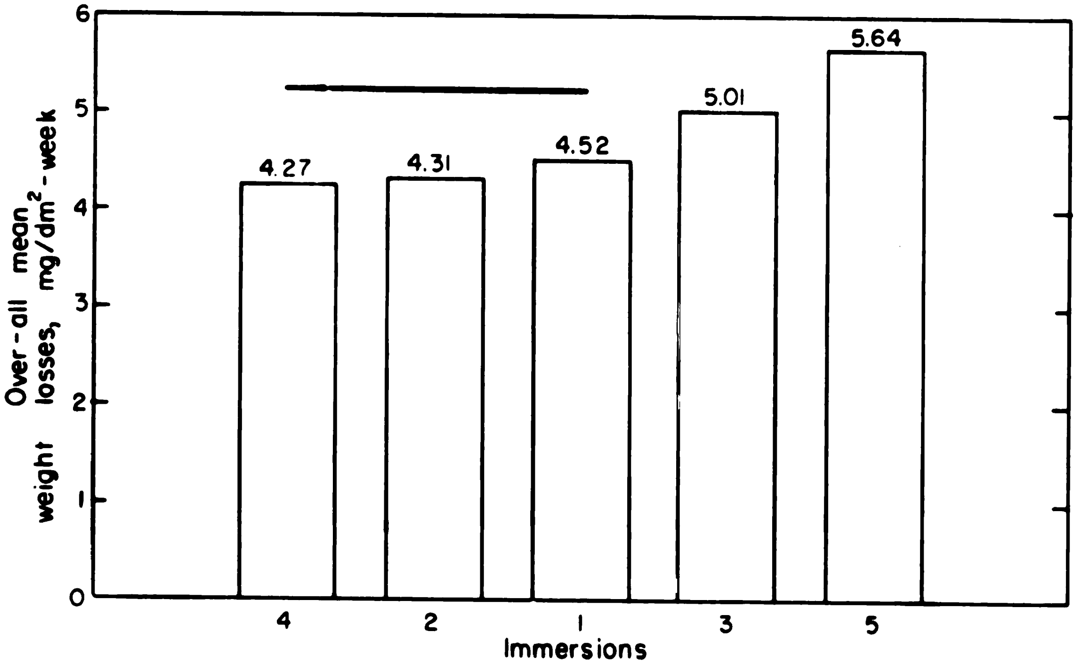

Fig. 17. **Comparison of the amount of corrosion obtained with different immersions of steel specimens in alkaline sequestering agent solutions made with hard water.**

effects of alkaline detergent, hard water sol-

Table 49. Macroscopic examination of the corrosion effects of alkaline detergent, hard water solutions on cold rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatment	Examination	Discoloration	Roughening	Local corrosion	Pitting	General corrosion	Total score	Percent of maximum total score
	Maximum score	3	4	9	12	12	40	100
3% Sodium hydroxide	Before CPR	1	4	9	12	6	32	80
	After CPR	2	4	8	12	9	35	88
3% Sodium hydroxide	Before CPR	2	4	9	12	9	36	90
+ 0.042% sodium gluconate	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide	Before CPR	3	4	9	12	11	39	98
+ 0.084% sodium gluconate	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide	Before CPR	3	4	9	12	11	39	98
+ 0.168% sodium gluconate	After CPR	3	4	9	12	12	40	100
3% Sodium hydroxide	Before CPR	2	4	7	12	12	37	92
+ 0.078% tetrasodium	After CPR	3	4	9	12	12	40	100
ethylenediaminetetraacetate								
3% Sodium hydroxide	BeforeCPR	2	4	7	12	12	37	92
+ 0.156% tetrasodium	After CPR	3	4	9	12	12	40	100
ethylenediaminetetraacetate								
3% Sodium hydroxide	Before CPR	2	4	7	12	12	37	92
+ 0.312% tetrasodium	After CPR	3	4	8	12	12	37	98
ethylenediaminetetraacetate								
3% Sodium hydroxide	Before CPR	2	4	8	12	10	36	90
+ 0.057% trisodium	After CPR	3	4	9	12	12	40	100
phosphate ($Na_3PO_4 \cdot 12H_2O$)								
3% Sodium hydroxide	Before CPR	2	4	8	12	10	36	90
+ 0.293% tetrasodium	After CPR	3	4	9	12	12	40	100
pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)								

Table 50. Macroscopic examination of the condition of the alkaline detergent, hard water solutions after immersion of cold rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatment	Examination	Cloudiness	Precipitate	General appearance	Total score	Percent of maximum total score
	Maximum score	4	8	8	20	100
3% Sodium hydroxide		3	6	6	15	75
3% Sodium hydroxide + 0.042% sodium gluconate		3	6	6	15	75
3% Sodium hydroxide + 0.084% sodium gluconate		3	6	7	16	80
3% Sodium hydroxide + 0.168% sodium gluconate		3	7	6	15	75
3% Sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate		3	7	7	17	85
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate		3	7	7	17	85
3% Sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate		3	7	7	17	85
3% Sodium hydroxide + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)		2	5	6	13	65
3% Sodium hydroxide + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)		3	6	6	15	75

Table 51. Over-all condition of the alkaline detergent, hard water systems expressed as a percentage of the maximum possible score for the sum of the solutions and the specimens in the systems before removal of the corrosion products. Mean values for five immersions data.

Treatment	Combined score, percent	Interpretation of the combined scores using the method of Darrin (1946)	
		Designation	Degree of corrosion
3% Sodium hydroxide	78	Fair	Questionable
3% Sodium hydroxide + 0.042% sodium gluconate	85	Good	Definite,but probably satisfactory
3% Sodium hydroxide + 0.084% sodium gluconate	92	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.168% sodium gluconate	90	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate	90	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate	90	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate	90	Good	Definite, but probably satisfactory
3% Sodium hydroxide + 0.057% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	82	Fair	Questionable
3% Sodium hydroxide + 0.293% tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	85	Good	Definite, but probably satisfactory

apparent. The A_I solutions caused slight discoloration and general corrosion of the specimens at the lower concentration and some slight general corrosion was apparent at the upper concentrations before corrosion products removal. No visual corrosion effects were apparent after removal of corrosion products. With A_{II} discoloration and local corrosion of the specimens were apparent before, but not after corrosion products removal, except some local corrosion was apparent at the upper A_{II} concentration. Discoloration, local and general corrosion of the specimens immersed in A_{III} and A_{IV} solutions were apparent before corrosion products removal but not after.

The condition of all the solutions employed in this study, which were made with hard water, were considerably poorer than the solutions employed in the previous study, which were made with distilled water. The 3% sodium hydroxide, A_I, and A_{IV} solutions tended to show similar appearances, with some solution cloudiness and precipitation. The A_{II} solutions exhibited less precipitation, less cloudiness and a better general appearance, while the A_{III} solutions exhibited the poorest over-all condition with considerable cloudiness and precipitation. The over-all condition of the systems evaluated is summarized in Table 51.

Distilled water and hard water studies combined and compared

Distilled water versus hard water

Corrosion weight loss results for steel specimens immersed in distilled water and hard water of 12 grains per gallon total hardness as calcium carbonate are presented in Table 52. An analysis of variance of the data is given in Table 53. The difference between the water over-all means was highly significant, with distilled water being the most corrosive. The immersion over-all means were ranked and tested for significant differences. Immersions 1, 2, and 3 which were not significantly different from each other were each significantly more corrosive than immersions 4 and 5, which were themselves not significantly different in over-all effect. Visual examination results for the specimens and solutions are presented in Tables 54, 55, and 56.

Distilled water, distilled water plus tetrasodium ethylenediaminetetraacetate, and hard water effects compared

The distilled water and hard water weight loss data of Table 52 and the distilled water + 0.156% tetrasodium ethylenediametetraacetate weight loss data of Table 22 were analyzed together by analysis of variance. The analysis of variance results are presented in Table 57. The agent and immersion over-all means are ranked in decreasing order and tested for significant differences in Table 58.

Alkaline detergent, distilled water and hard water studies combined and compared

The nine alkaline detergent solutions made with distilled water can be compared with each other and with the nine alkaline detergent solutions made with 12 grain per gallon hard water by an analysis of variance procedure which treats these solutions as 18 different solutions (or agents) if homogeneity of variance exists between the two sets of data. The

Table 52. Corrosion weight loss results of cold rolled AISI No. C 1008 steel specimens immersed in water for one week (7 days).

Agents	Mean weight loss, mg/dm^2-week					
	Immersions					Agent over-all means
	1	2	3	4	5	
Distilled water	139.33	145.65	138.20	124.33	128.43	135.19
Hard water, 12 grains per gallon	120.33	123.95	120.80	105.50	95.95	113.31
Immersion over-all means	129.83	134.80	129.50	114.91	112.19	124.25

Table 53. Analysis of variance of corrosion weight loss data for steel specimens immersed in distilled water and hard water of 12 grains per gallon total hardness as calcium carbonate.

Source	Degrees of freedom	Sum of squares	Mean square	F
Total	39	12544.56		
Immersions[1]	4	3221.11	805.28	5.70**
Agents	1	4787.35	4787.35	33.90**
Interaction	4	299.96	74.99	0.53
Error	30	4236.14	141.20	

**Significant, 1% level.

[1] Denotes distilled water and hard water.

sampling error variance of the distilled water solution data (from Table 27) was compared to the sampling error variance of the hard water solution data (from Table 27) by Cochran's Test for homogeneity of variance (Dixon and Massey (1957)). Cochran's Test showed that the hypothesis of equal variances should be rejected at the 1% level of significance (the calculated value was 0.6448 and the critical value for rejection at the 1% level was 0.6146). Since homogeneity of variance was not found at the 1% level of significance for these two sets of data one can not combine or analyze the two sets of data together without invalidating to some extent the analysis of variance test for means. However, in order to allow approximate comparisons of the various treatments the data was combined and analyzed together. The analysis of variance results are presented in Table 59. The agent over-all means are ranked and tested for significant differences in Table 60. These results are to be interpreted as approximate only and the conclusions weighted accordingly.

Concentration effects of sequestering agents in alkaline distilled water and hard water solutions.

The sequestering agent concentration effects in alkaline distilled water and hard water solutions are presented here to facilitate direct comparisons between these two systems. Analysis of variance results for each agent and water type-solution are presented in Table 61. The concentration and immersion over-all means are ranked in decreasing order and tested for significant differences in Table 62.

The effect of sequestering agent concentration on the corrosiveness

Table 54. Macroscopic examination of the corrosion effects of distilled water and hard water on rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatment	Examination	Discoloration	Roughening	Local corrosion	Pitting	General corrosion	Total score	Percent of maximum total score
	Maximum score	3	4	9	12	12	40	100
Distilled water	Before CPR	0	3	9	11	1	24	60
	After CPR	1	4	9	12	4	30	75
Hard water, 12 grains per gallon	Before CPR	0	3	9	11	1	24	60
	After CPR	1	4	9	12	5	31	78

Table 55. Macroscopic examination of the condition of the distilled water and hard water solutions after immersion of cold rolled AISI No. C 1008 steel specimens. Mean values for five immersions data.

Treatment	Examination	Cloudiness	Precipitate	General appearance	Total score	Percent of maximum total score
	Maximum score	4	8	8	20	100
Distilled water		0	1	0	1	5
Hard water, 12 grains per gallon		1	2	1	4	20

Table 56. Over-all condition of the system expressed as a percentage of the maximum possible score for the sum of the solution and the specimens in the system before removal of the corrosion products. Mean values for five immersions data.

Treatment	Combined score, percent	Interpretation of the combined scores using the method of Darrin (1946)	
		Designation	Degree of corrosion
Distilled water	40	Bad	Severe corrosion
Hard water, 12 grains per gallon	47	Bad	Severe corrosion

Table 57. Analysis of variance of corrosion weight loss data for steel specimens immersed in distilled water, 12 grain per gallon hard water and distilled water plus 0.156% tetrasodium ethylenediaminetetraacetate.

Source	Degrees of freedom	Sum of squares	Mean square	F
Total	59	25620.98		
Immersions	4	5550.26	1387.57	14.31**
Agents	2	14859.68	7429.84	76.64**
Interaction	8	848.09	106.01	1.09
Error	45	4362.95	96.95	

**Significant, 1% level.

Table 58. Comparison of the amount of corrosion of steel specimens immersed in distilled water, 12 grain per gallon hard water, and distilled water + 0.156% tetrasodium ethylenediaminetetraacetate.

Agents	Agent over-all means, mg/dm^2-week	Immersions	Immersion over-all means, mg/dm^2-week
Distilled water + 0.156% tetrasodium ethylenediaminetetraacetate	151.73	2	143.54
		1	142.34
Distilled water	135.19	3	136.64
Hard water, 12 grain per gallon	113.31	4	125.48
		5	119.03

Table 59. Analysis of variance of corrosion weight loss data for steel specimens immersed in alkaline detergent solutions made with distilled water and 12 grain per gallon hard water.

Source	Degrees of freedom	Sum of squares	Mean square	F
Total	359	1316.28		
Immersion	4	62.06	15.52	56.42**
Agents	17	943.05	55.48	201.73**
Interaction	68	236.89	3.48	12.67**
Error	270	74.28	0.275	

**Significant, 1% level.

of alkaline sequestering agent solutions can be assessed analytically by determining the regression of weight loss on concentration. The concentration data for each agent and water type were analyzed for the following: (1) regression, (2) linearity of regression, and (3) when linearity of regression was found, the linear regression predicting equation was determined. The results are presented in Table 63. The variation in corrosion weight loss as affected by concentration of sequestering agent (sodium gluconate or tetrasodium ethylenediaminetetraacetate) in 3% sodium hydroxide solutions made with either distilled water or 12 grain per gallon hard water is shown in Figures 18, 19, 20 and 21.

Table 60. Comparison of the amount of corrosion of steel specimens immersed in alkaline sequestering agent solutions made with distilled water or 12 grains per gallon hard water.

Agent codes	Agents	Agent over-all means, mg/dm^2-week
22C1	Hard water + 3% sodium hydroxide + 0.042% sodium gluconate	8.57
22C2	Hard water + 3% sodium hydroxide + 0.084% sodium gluconate	7.21
22C4	Hard water + 3% sodium hydroxide + 0.168% sodium gluconate	6.63
11	Hard water + 3% sodium hydroxide	4.13
3C4	Distilled water + 3% sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate	3.57
2C4	Distilled water + 3% sodium hydroxide + 0.168% sodium gluconate	3.51
55	Hard water + 3% sodium hydroxide + 0.293% tetrasodium pyrophosphate·10 water	3.49
3C2	Distilled water + 3% sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate	3.43
33C2	Hard water + 3% sodium hydroxide + 0.156% tetrasodium ethylenediaminetetraacetate	3.33
2C2	Distilled water + 3% sodium hydroxide + 0.084% sodium gluconate	3.28
44	Hard water + 3% sodium hydroxide + 0.057% trisodium phosphate·12 water	3.25
2C1	Distilled water + 3% sodium hydroxide + 0.042% sodium gluconate	3.18
33C1	Hard water + 3% sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate	3.15
5	Distilled water + 3% sodium hydroxide + 0.293% tetrasodium pyrophosphate·10 water	3.14
3C1	Distilled water + 3% sodium hydroxide + 0.078% tetrasodium ethylenediaminetetraacetate	3.13
33C4	Hard water + 3% sodium hydroxide + 0.312% tetrasodium ethylenediaminetetraacetate	3.01
4	Distilled water + 3% sodium hydroxide + 0.057% trisodium phosphate·12 water	3.00
1	Distilled water + 3% sodium hydroxide	2.74

Table 61. Analysis of variance of corrosion weight loss data for steel specimens immersed in distilled water and 12 grain per gallon hard water solutions of 3% sodium hydroxide plus sodium gluconate and 3% sodium hydroxide plus tetrasodium ethylenediaminetetraacetate (each sequestering agent used at three concentration levels).

Source	Waters							
	Distilled water				Hard water, 12 grains per gallon			
	Degrees of freedom	Sum of squares	Mean square	F	Degrees of freedom	Sum of squares	Mean square	F
3% Sodium hydroxide + sodium gluconate								
Total	59	34.20			59	83.75		
Immersions	4	21.99	5.50	48.65**	4	22.54	5.64	19.17**
Concentrations	2	1.12	0.560	4.96*	2	39.67	19.84	67.47**
Interaction	8	6.02	0.753	6.66**	8	8.29	1.04	3.52**
Error	45	5.07	0.113		45	13.25	0.294	
3% Sodium hydroxide + tetrasodium ethylenediaminetetraacetate								
Total	59	132.58			59	50.06		
Immersions	4	106.82	26.71	74.18**	4	24.48	6.12	12.97**
Concentrations	2	2.04	1.02	2.83*	2	1.00	0.500	1.06
Interaction	8	7.50	0.938	2.61*	8	3.35	0.419	0.888
Error	45	16.22	0.360		45	21.23	0.472	

*Significant, 5% level.

**Significant, 1% level.

Table 62. Comparison of the amount of corrosion of steel specimens immersed in alkaline sequestering agent solutions of different concentrations made with distilled water and 12 grain per gallon hard water.

Agents	Waters			
	Distilled water		Hard water, 12 grains per gallon	
	Concentration of sequestering agent, percent	Concentration over-all means, mg/dm^2-week	Concentration of sequestering agent, percent	Concentration over-all means, mg/dm^2-week
3% Sodium hydroxide + sodium gluconate	0.168	3.51	0.042	8.57
	0.084	3.28	0.084	7.21
	0.042	3.18	0.168	6.63
3% Sodium hydroxide + tetrasodium ethylenediaminetetraacetate	0.312	3.57	0.156	3.33
	0.156	3.43	0.078	3.15
	0.078	3.13	0.312	3.01

Table 63. Analysis of regression of corrosion weight loss (Y) on the concentration of sequestering agent (X).

Agents	Test for, H: $\rho YX = 0$	Test for, H: Linearity of regression	*Estimated linear regression equations
Distilled water			
3% Sodium hydroxide + sodium gluconate	Accept at $\alpha = 0.05$ Reject at $\alpha = 0.20$	Accept at $\alpha = 0.05$	$\tilde{Y} = 3.065 + 2.601X$
3% Sodium hydroxide + tetrasodium ethylenediaminetetraacetate	Accept at $\alpha = 0.05$ Reject at $\alpha = 0.40$	Accept at $\alpha = 0.05$	$\tilde{Y} = 3.057 + 1.735X$
Hard water, 12 grains per gallon			
3% Sodium hydroxide + sodium gluconate	Reject at $\alpha = 0.01$	Accept at $\alpha = 0.05$	$\log Y = 0.7782 + \frac{0.006442}{X}$
3% Sodium hydroxide + tetrasodium ethylenediaminetetraacetate	Accept at $\alpha = 0.05$ Accept at $\alpha = 0.50$	———	———

H: $\rho YX = 0$; Test for the hypothesis that the regression coefficient is zero for the population.

α; The level of significance.

*General equations of $\tilde{Y} = a + b_{yx}X$ or $\log \tilde{Y} = a + \frac{b_{YX}}{X}$ type.

$\tilde{Y}$; The estimate of an unknown Y from a known X.

a; The Y- intercept.

b_{YX}; The slope of the line or the linear regression coefficient of Y on X.

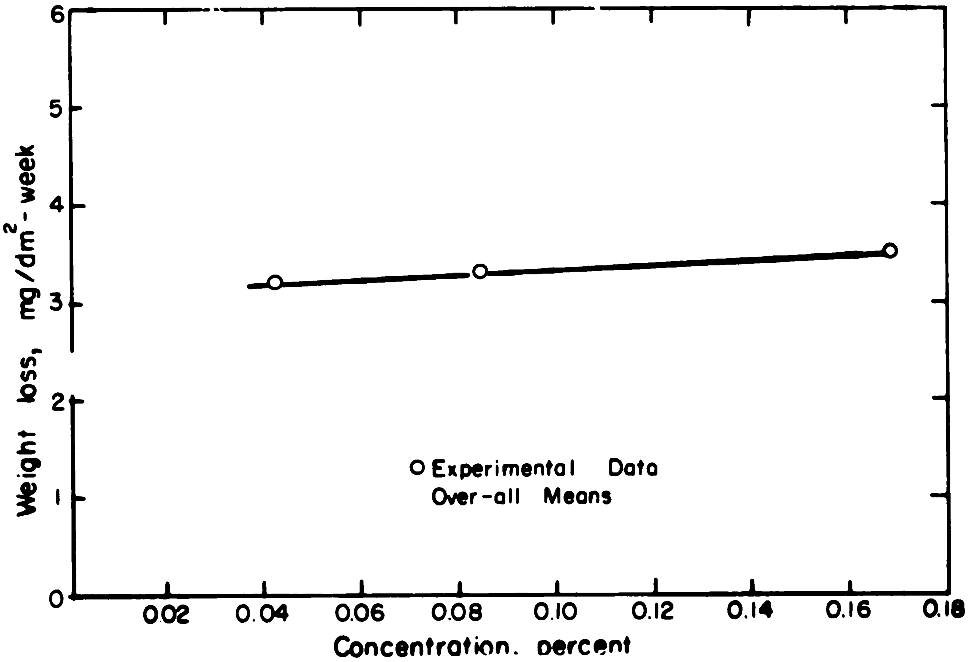

Fig. 18. Corrosion weight loss of steel specimens immersed in alkaline solutions made with distilled water and containing different concentrations of sodium gluconate. The estimated linear regression line (weight loss versus concentration) is drawn.

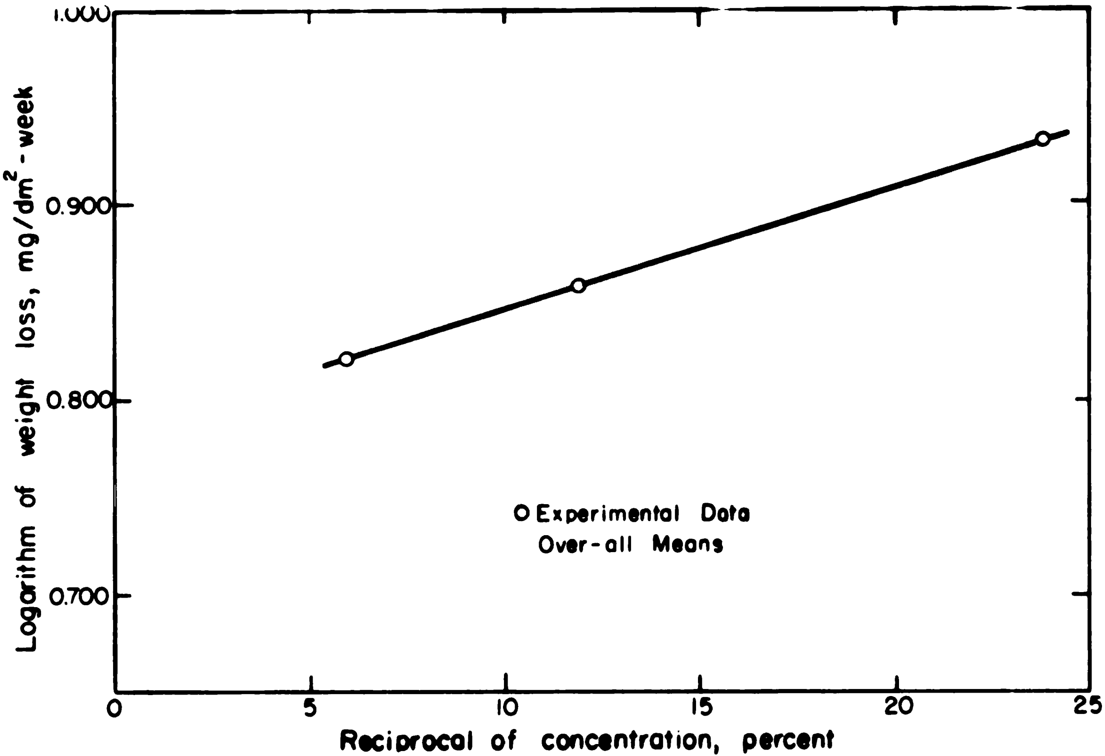

Fig. 19. Corrosion weight loss of steel specimens immersed in alkaline solutions made with 12 grain per gallon hard water and containing different concentrations of sodium gluconate. The estimated linear regression line (log of weight loss versus reciprocal of concentration) is drawn.

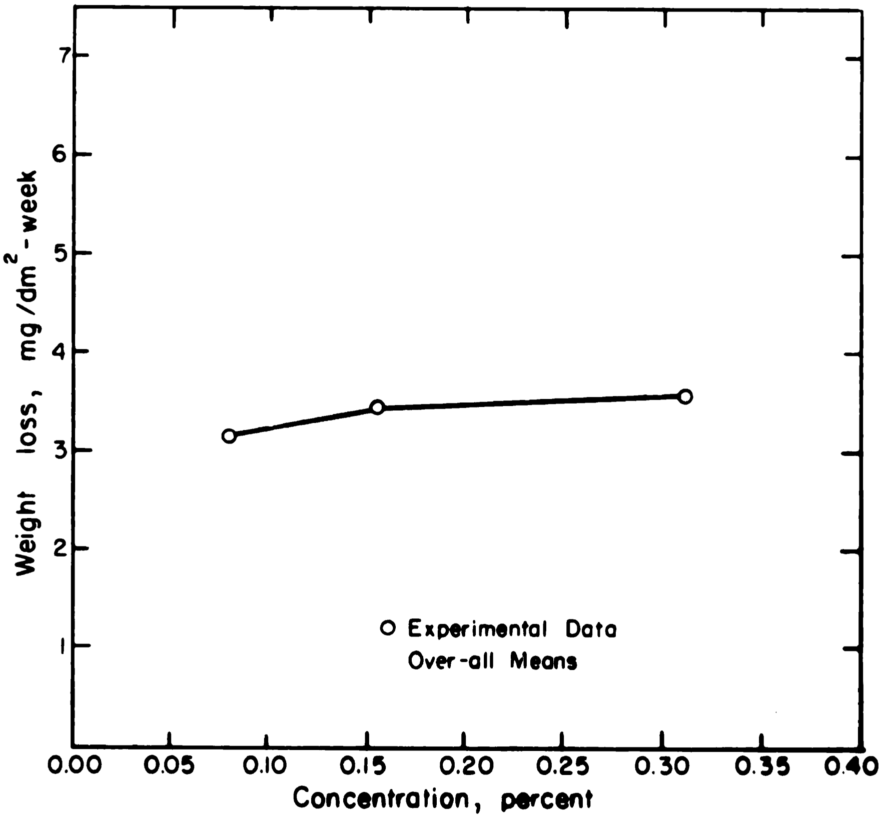

Fig. 20. Corrosion weight loss of steel specimens immersed in alkaline solutions made with distilled water and containing different concentrations of tetrasodium ethylenediaminetetraacetate.

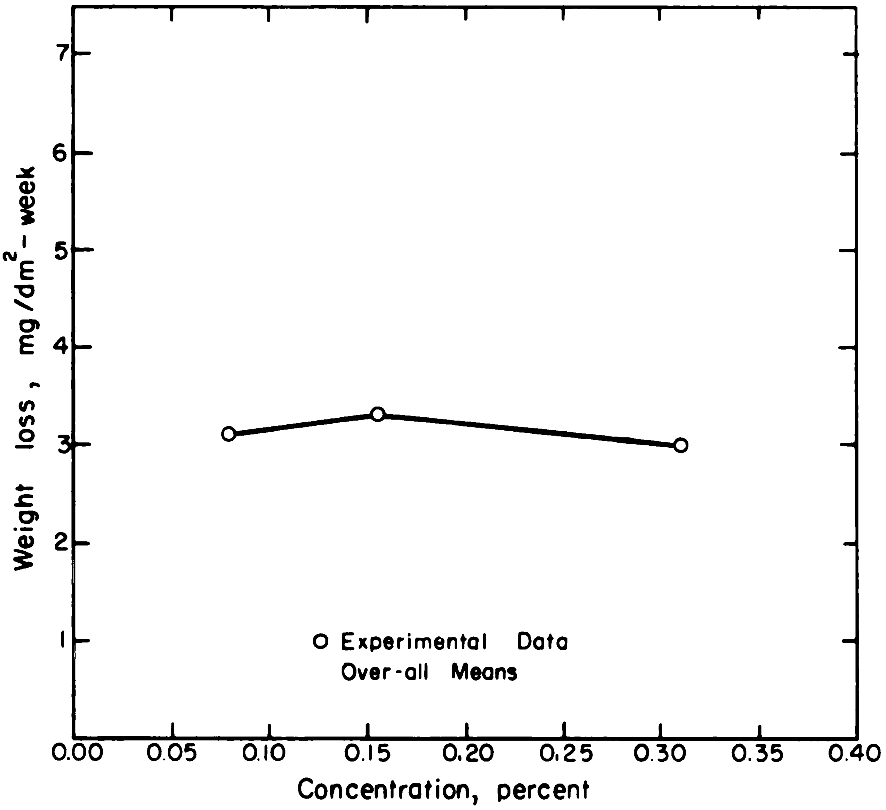

Fig. 21. Corrosion weight loss of steel specimens immersed in alkaline solutions made with 12 grain per gallon hard water and containing different concentrations of tetrasodium ethylenediaminetetraacetate.

DISCUSSION OF RESULTS

The problem under investigation was the determination of the corrosion inhibiting or accelerating effects of organic sequestering agents, one of the hydroxycarboxylic acid type and one of the aminopolycarboxylic acid type, relative to the effects of the more traditionally used inorganic phosphates and the other components of the system (water, alkali, and hardness-forming salts in water), under conditions similar to and varied in accordance with what is commonly encountered in their use in cleaning reusable glass containers in mechanical washing machines.

Studies on materials and methods

Materials

In the experiment to determine the susceptibility to corrosion of cold rolled and hot rolled steel (AISI No. C 1008) in distilled water it was determined that the difference in amount of corrosion obtained with the two steels was highly significant (1% probability level of significance), with cold rolled steel found the most susceptible to corrosion. It was also determined that no significant difference (5% probability level of significance) existed between the two steels in the alkaline solutions. Since the agent, immersion, and interaction effects are of secondary interest at this point their discussion will be delayed until the distilled water-sodium hydroxide-sequestering agent section.

The difference in results for water and for the alkaline solutions could be explained as follows: In both cases a maximum of no greater than 6.78 ml of oxygen could become available for reduction at the cathodes. A maximum oxygen availability of 6.78 ml could theoretically account for about 33.8 mg of iron being corroded to the ferrous state. In cases where 6.78 ml of oxygen is available for reduction, and the corrosion obtained does not exceed to any great extent the 33.8 mg corrosion of iron, the corrosion would be classified as predominately oxygen-type corrosion. In cases where the corrosion greatly exceeds this value the corrosion would be classified as predominately hydrogen-type corrosion.

The grand over-all means for the steels in distilled water and in the alkaline solutions were 136.31 and 3.67 mg/dm^2-week, respectively. It appears then that hydrogen-type corrosion predominates in the former and oxygen-type corrosion predominates in the latter. Uhlig (1948) in his review and discussion of the effect of cold working on iron and steel corrosion pointed out the following: Cold working has no appreciable effect when oxygen diffusion controls the corrosion rate, but when corrosion is by hydrogen evolution a definite effect of heat treatment employed to relieve internal stresses, results in decreased corrosion. Johnson (1946), Speller (1935), and Evans (1960) have also reviewed and discussed the effects of cold working on corrosion of metals. They note that the corrosion rate of iron and steel is accelerated by cold working, particularly if the cold deformation is localized and that the action of chemicals upon strained and unstrained metals is different. Evans states that straining can greatly increase corrosion velocity and that the strained metal acts as a more reactive material than the annealed metal. Speller states that the effect of strain may be due to variations in surface-film protection, caused by the breaking of the film on certain areas, or to differences in surface finish of the strained areas, or to differences in grain distortion. Johnson, Speller and Evans did not make any distinction between effects of cold working in hydrogen-type and oxygen-type corrosion as did Uhlig.

The results reported here are consistant with Uhlig's interpretation of cold working effects on iron and steel, undergoing either hydrogen-type or oxygen-type corrosion. The distilled water results in which hydrogen-type corrosion appears to predominate showed a highly significant difference, with cold rolled steel experiencing the greatest amount of corrosion. In the case of the alkaline solutions' results, in which oxygen-type corrosion appears to predominate, no significant difference between the steels was found.

Based on the findings, that the steel means were not significantly different in alkaline solutions similar to those to be studied in this investigation, it was decided to use one type of steel. Since the cold rolled steel specimens had more uniform dimensions and were easier to prepare for testing (degreasing and pickling) they were selected.

Methods

It was determined that different individuals could reproduce experiment results (when the 5% probability level of significance was used as the criteria of reproducibility) using the experimental procedure to be employed in the subsequent studies. It should be noted that individuals B and C both had a college degree and considerable training in chemistry and chemical techniques. Individual A on the other hand did not have a college degree, but did have some chemistry training and some laboratory technician experience. One might, in the opinion of the author, state that individuals B and C demonstrated a higher degree of interest and conscientiousness relative to the studies, as well as better laboratory techniques than individual A. This opinion appears to be justified by the fact that individuals B and C had considerably lower and quite similar values for their individual over-all standard deviations and mean errors than individual A. Despite these differences, the results obtained with these individuals were not significantly different and it would appear then that the experimental procedure as developed has merit with regard to the above.

Studies on distilled water-sequestering agent systems

It has been determined that marked differences exist in the effects of various types of sequestering agents on the corrosion of mild steel. While sequestering agents are not usually used in systems as simple as these in practice, knowledge of their behavior here is basic to explaining the behavior of sequestering agents in the more complex systems of practical importance. Distilled water solutions of phsophates (trisodium phosphate, A_{III}, and tetrasodium pyrophosphate, A_{IV}), a hydroxycarboxylate (sodium gluconate, A_{I}) and an aminopolycarboxylate (tetrasodium ethylenediaminetetraacetate, A_{II}) resulted in 2.39, 25.1, and 112 percent as much corrosion as distilled water (Table 52), respectively. It is obvious that the differences in corrosion between these solutions and distilled water are highly significant, except in the case of the aminopolycarboxylate, A_{II}. A statistical comparison (presented in Tables 57 and 58) has shown A_{II} to be significantly more corrosive than distilled water alone. The concentrations and ionic strengths, μ , (μ presented in parenthesis) of the solutions used in units of molality, m, (moles of solute per 1000 g of solvent) were for A_{I} 0.0039m (0.0039m), for A_{II} 0.0041m (0.041m), for A_{III} 0.0015m (0.009m) and for A_{IV} 0.0066m (0.066m). These concentrations represent the commercially recommended quantities of agents for softening water of 12 grains per gallon hardness. These "use concentrations" were employed in all comparisons of agent effects in each phase of this investigation, except where concentration effects themselves were under study. In the case where concentration effects were under study the levels used were one-half, one, and two times the use concentrations. The use concentration represents, in the case of A_I and A_{II} a sequesteration ratio of 2 moles of sequestering agent per mole of metal ions to be sequestered. For A_{III} and A_{IV} the ratios were 0.73:1 and 3.2:1 respectively.

The discussion and explanation of results will be of a general rather than a specific nature because of the limited information available on the behavior of these agents in these systems and under the conditions of interest. For example, chelate formation or stability constant values needed are generally unknown except for simplified systems and limited conditions. In addition, the lack of specific qualitative and quantitative information on the nature and distribution of corrosion products, imposes some restrictions on the degree of certainty that can be attached to the reactions and explanations proposed in the following discussions. An attempt is made, however, to present what seem to be reasonable explanations for the findings based on certain well known relationships. The effects of precipating agents on metal chelates (or sequestering agents on metal precipitates may be expressed in general by the following equilibrium (Chaberek and Martell (1959)):

$$MA + B \underset{K_{x'}}{\overset{K_x}{\rightleftarrows}} MB\downarrow + A$$

where A is a sequestering agent and B is a precipitating agent, which combine with the metal to give the soluble chelate MA and precipitate MB respectively. The exchange constant K_x is related to K_{MA}, the metal chelate formation constant, and K_{MB}, the solubility product of MB, by the equation $K_x = \frac{1}{K_{MA}K_{MB}}$. Thus the tendency toward precipitation of the insoluble metal salt, measured by K_x, is a function of both the solubility product and the metal chelate formation constant. The precipitation of MB may be prevented if K_x is sufficiently small. The equilibrium constant for the reverse reaction, $K_{x'}$, measures the tendency of the chelating agent to solubilize the slightly soluble salt MB and is equal to the reciprocal of K_x.

Further discussion of results will be by the individual types of sequestering agents studied.

Sodium gluconate, A_I(hydroxycarboxylate)

Sodium gluconate is not an effective sequestering agent for ferrous or ferric ions in distilled water of pH 7 (Mehltretter, Alexander, and Rist (1953)). The approximate value of $K_{x'}$ is equal to the product of $1.1x10^{-36}$, the ferric hydroxide solubility product constant at 18°C, and $3.16x10^{-6}$, the gluconate-ferric metal chelate formation constant at 25°C (the gluconate-ferrous metal chelate formation constant was not given in Chaberek and Martell's (1959) tabulation of reported chelate formation constants), giving $3.48x10^{-42}$ which would predict that ferric hydroxide would not be solubilized. It is thus evident that the reaction or equilibrium for

$$MA_I + B \underset{K_{x'}}{\overset{K_x}{\rightleftharpoons}} MB\downarrow + A_I$$

would lie predominately to the right. Since sodium gluconate does not tend to solubilize (sequester) these ions, it might be expected that the amount of corrosion would be near the value for distilled water alone. However, such was not the case, and about 75 percent less corrosion was found with sodium gluconate in distilled water than with distilled water alone. It appears then that the sodium gluconate is functioning as a hydrogen-type corrosion inhibitor (by controlling hydrogen evolution). The supporting evidence is that the amount of corrosion (33.88 mg/dm^2-week) found did not appreciably exceed the amount accountable for on the basis of the calculated maximum amount of oxygen present. Since the amount of weight loss found is approximately equal to the maximum for oxygen-type corrosion it is expected that oxygen-type corrosion predominated. The addition of A_I to distilled water would increase its pH. By increasing the pH (increasing OH^- ion concentration) the solubility of the ferrous hydroxide would be decreased. By decreasing the ferrous hydroxide solubility some corrosion inhibition would be expected in oxygen-type corrosion, since the ferrous hydroxide surface film of corrosion products tends to decrease oxygen diffusion rate to the cathodes. Undoubtedly hydrogen-type corrosion predominated in the case of distilled water, since the amount of corrosion found so greatly exceeded that accountable for on the basis of the maximum oxygen (6.78 ml) available for reduction. It would seem from the above that sodium gluconate may be functioning as a corrosion inhibitor, by limiting hydrogen evolution, which is the major corrosion rate controlling factor in hydrogen-type corrosion.

Evans (1960) with the aid of the literature has put forward some tentative explanations of the corrosion inhibition mechanisms involved here. He has pointed out that in the case of hydroxycarboxylic acids, the hydroxyl groups may help anchor the anions, which once they reach the metal surface are likely to be held fast. He notes two possibilities pertaining to removal from the surface: first the removal of the organic anion with metal attached, forming a complex anion or second the removal of the radical, leaving oxygen behind, as in the case of chromate. According to Evans, which of these occurs, probably depends on the relative strengths of the chemical bonds which must be broken if complex-anion formation (leading to corrosion) or oxide-formation (leading to passivity) is to be obtained, and without knowledge of bond strengths, prophecy is difficult. Evans also points out that certain organic compounds result in decreased corrosion rate and this decrease has been attributed to adsorption of the compound on the metal surface. He notes that the molecules tend to attach themselves at points where the greatest free force-field exists to attract them, and that these are generally the places where corrosion would tend to start. As a result inhibition of corrosion may occur.

From the above it is apparent that at least two mechanisms of corrosion inhibition exist which would tend to explain the decreased corrosion found with distilled water plus sodium gluconate as compared to that of distilled water.

The results reported here tend to agree with those of a previous study by Nieland, Maguire, George, and Kahler (1950_b) where their interest centered on flow and corrosion in iron pipes. They reported 84 percent protection with 0.084 percent sodium gluconate in Philadelphia tap water of 42 ppm total hardness as $CaCO_3$ at $120^{o}F$ and flowing at 3.5 ft/sec, while we found 75 percent protection with distilled water at $150^{o}F$ under essentially static conditions. The smaller amount of hardness, lower temperature, and flow could have contributed to the greater degree of protection obtained in the Nieland, Maguire, George and Kahler study. The visual examination data for the two studies tend to agree, since in both instances a dark, hard, corrosion products film was observed and pitting was reported at the gluconate concentration used in this study.

It appears from the above that sodium gluconate could serve as a useful inhibitor of mild steel corrosion in distilled water. Nieland, Maguire, George, and Kahler (1950_b) found corrosion protection with hydroxycarboxylic acids in waters of greater hardness, but pointed out that care must be exercised in selection of the concentration to be used, since high concentrations may product pitting. However, they noted that the percent protection tended to decrease as the water hardness increased.

Tetrasodium ethylenediaminetetraacetate, A_{II} (aminopolycarboxylate)

Addition of tetrasodium ethylenediaminetetraacetate (0.156 percent) to distilled water resulted in a significant increase in corrosion. The over-all mean weight loss was 12 percent greater with A_{II}, than without it. An increase in the amount of corrosion was expected since it is known that A_{II} is an effective sequesterant for ferrous ions at about pH 7. Solubilization of the corrosion products is predicted by the product of the ferrous hydroxide solubility product constant of 1.64×10^{-14} at $18^{\circ}C$ and A_{II}-ferrous metal chelate formation constant of 2.15×10^{14} at $20^{\circ}C$. The product of these two values gives $K_{x'}$ value of 3.53, which would indicate that sequestration (or solubilization) of the ferrous hydroxide should occur to some extent under these conditions. The equilibrium for the following reaction would then tend to lie to the left, favoring some formation of the metal chelate (MA_{II})

$$MA_{II} + B \underset{K_{x'}}{\overset{K_x}{\rightleftharpoons}} MB\downarrow + A_{II}$$

from the metal hydroxide (MB). A theoretical maximum of 0.1145 g of iron could be sequestered with 500 ml of 0.0041m A_{II} solution. The results of the study showed an added metal weight loss of about 16.5 mg/dm^2-week. The data above tends to indicate some sequestration of the corrosion products if the action of A_{II} is confined to that portion of the corrosion which was predominately oxygen-type. Sequestration can produce increased corrosion by decreasing the amount or thickness of the corrosion products film on the surface, which will increase the rate of oxygen diffusion to the cathodes, resulting in an increased amount of corrosion. The ferrous hydroxide corrosion products film is the primary corrosion rate controlling factor in oxygen-type corrosion; however, hydrogen evolution is the primary corrosion rate controlling factor in hydrogen-type corrosion. Since hydrogen-type corrosion was the predominate type of corrosion (occurring after the more spontaneous oxygen-type corrosion) the possibility of A_{II} causing the increased corrosion by functioning in some manner that would affect the rate of hydrogen evolution from the metal surface also exist. It seems somewhat preferable to accept the explanation that the A_{II} participates and functions to increase corrosion by ferrous ion sequestration during the oxygen phase of corrosion. If the effect of A_{II} was limited to the oxygen phase of the corrosion (maximum weight loss accountable for on the basis of the maximum oxygen available in these systems is 33.8 mg) then the 16.5 mg weight loss represents an increase of about 50 percent during the oxygen phase of the corrosion. It is entirely possible that A_{II} may have affected both phases of the corrosion in a positive manner (increasing corrosion) or by affecting the oxygen corrosion phase by a greater positive manner than suspected and then countered with a negative effect during the hydrogen corrosion phase such as to have given a net increase in corrosion of the 12 percent found. It obviously can not be stated how the agent produced the given effect, but it seems somewhat more reasonable to suspect that the increase occurred during the oxygen phase of corrosion.

With regard to the visual examination results obtained in this system two particular observations were noted: The first was the very noticable dark red-to-brown colored corrosion products (also pink-to-purplish tint in some cases) on the specimens and in the solutions. This noticeably different color for the A_{II} solutions, from that obtained with the distilled water solutions, probably represents the color of the metal complex formed. It is known (Chaberek and Martell (1959)) that such complexes exhibit various colors dependent upon experimental conditions. The second observation of interest was the adherence of these colored corrosion products to the metal surface. It was very difficult to remove these films with the prescribed corrosion products removal process used throughout these studies. A visibly small amount of the corrosion products could not be removed after each successive immersion and the amount that remained seemed to increase with successive immersions. This difficulty was apparently responsible for the decrease in weight loss data found with each successive immersion.

It would appear from the above that A_{II} should not be used with soft water in equipment fabricated with mild steel without considering the increased corrosion that could result. No studies were conducted with hard water solutions of A_{II}. However, it seems reasonable to expect a corrosion rate between that for the distilled water plus A_{II} and that for distilled water alone; perhaps this value would be closest to the lower distilled water value. The basis for this expectation is that at least some of the A_{II}, if not all of it, would be involved or tied up in calcium and magnesium chelates and the free A_{II} available to function as a corrosion accelerator would be decreased.

Trisodium phosphate and tetrasodium pyrophosphate, A_{III} and A_{IV} (phosphates)

The over-all mean weight loss found with the phosphates was about 97.6 percent less than that for distilled water. This reduction in corrosion is attributed to anodic corrosion inhibition. The concentration of phosphate anions (0.0015m, A_{III} or 0.0066m, A_{IV}) was considerably greater than the hydroxyl anion concentration (about 10^{-7} moles per liter for water). As a result the product of the oxidation reaction (ferrous ion) can readily combine with phosphate ion, and since these iron-phosphates are insoluble they are immediately precipitated directly on or in close proximity to the anodes. This results in anodic corrosion inhibition (Evans (1960)). The product of the cathodic reaction, sodium hydroxide, is soluble. The over-all reactions might theoretically be demonstrated as follows:

$$6Fe + 4Na_3PO_4 + 3O_2\uparrow + 6H_2O = 2Fe_3(PO_4)_2\downarrow + 12NaOH$$

$$2Fe + Na_4P_2O_7 + O_2\uparrow + 2H_2O = Fe_2P_2O_7\downarrow + 4NaOH$$

The appearance of the specimens and solutions was the same both before and after immersion in the phosphate solutions. However, it is known that ferrous-phosphates are white-to-blue in color, and this along with the small quantity of corrosion products formed was probably responsible for making their detection difficult, and the general observation of no visible corrosion.

The fact that phosphates decrease the corrosivity of water under various conditions is well known by corrosion experts (Speller (1935) and Evans (1960)), but is not so well known by beverage industry personnel. This study serves to compare the relative effects of these four agents on a quantitative basis which has not previously been done.

On the basis of these results one might reasonably expect that the use of these agents in water rinse sections of a washer could result in reduced corrosion, particularly if more phosphate than that required to soften the water was used. It is known that calcium-phosphate complexes can act as effective corrosion inhibitors (according to Evans (1960)). The mechanism by which they inhibit corrosion has been described as a cathodic one (Putilova, Balezin, and Barannik (1960)). They reported that glassy phosphates, for instance, migrate towards the cathodes in water containing calcium ions and that this differs sharply from the behavior of phosphates in distilled water, where they move toward the anodes. They attributed the migration to the cathodes as due to positively charged colloidal particles consisting of numerous diphosphate chains joined by calcium atoms and pointed out that the positive charge on the colloidal particles may be due to adsorption of calcium ions by colloidal calcium phosphate.

Studies on distilled water-sodium hydroxide-sequestering agent systems

Agent effects

The corrosion weight loss value of 2.74 mg/dm^2-week (or 0.07 mils/yr) found with the 3% sodium hydroxide control compares well with the reported literature value of about 0.1 mil/yr for studies on mild steel conducted under similar test conditions (Uhlig (1948) and Speller (1951)).

Trisodium phosphate, A_{III} (4), was not significantly more corrosive than the control (1). Tetrasodium pyrophosphate, A_{IV} (5), sodium gluconate, A_I (2C2), and tetrasodium ethylenediaminetetraacetate, A_{II} (3C2) listed in order of increasing corrosivity were each significantly more corrosive than the control. In 3% sodium hydroxide solutions an insoluble layer of corrosion products, $Fe(OH)_2$, will be readily formed. The solubility of ferrous hydroxide decreases from about 3.8 ppm to about

0 ppm (or nil) as the pH increases from 7 to 12 (Speller (1951)).

The effect of the above mentioned agents can be explained as follows: In a 3% sodium hydroxide solution the equilibrium for the reaction

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

lies predominately to the left; however the ferrous ions in solution can be complexed by the A_I, A_{II}, A_{III}, and A_{IV} anions and form either soluble or insoluble complexes, thus tying up the free ferrous ions which will be replaced by ionization of $Fe(OH)_2$ to re-establish the equilibrium. The above process should continue as long as sufficient complexing agent remains. As a result of these reactions the nature and distribution of the corrosion products can be modified to such an extent that the over-all corrosion rate may be significantly increased or decreased. Apparently the A_{III} did not appreciably modify the nature and distribution of corrosion products by perhaps ferrous-phosphate formation and combination with the corrosion products, and/or by precipitation of ferrous-phosphate at a distance from the metal surface and the settling of the complex to the bottom of the container. The A_{IV} on the other hand did apparently have a significant effect through modification of the nature and distribution of corrosion products. Sodium gluconate's significant increase in corrosion over that obtained with the control would appear to be due to the fact that A_I forms stable, water soluble iron chelates in alkaline solutions (Mehltretter and Watson (1953)). On the other hand, it is reported that A_{II} is not effective as a sequestering agent for ferrous ions above pH 12 ("Keys to Chelation" (1959)); however, it was the only agent found significantly more corrosive than both the control and the A_{III} solution. Apparently even at a pH of 13.8 the A_{II} possesses sufficient sequestering power for ferrous ions to cause this increase, or the increase is due to some other effect. It can also be observed from the results that the three sequestering agents (A_I, A_{II} and A_{IV}) produced significantly more corrosion than the control, while the non-sequestering agent A_{III} did not. Further, there seems to be a tendency exhibited by the agent over-all means to indicate more corrosion with organic sequestering agents than with the inorganic agents in this system and for the agents tested.

The analysis of the alkaline detergent, distilled water solution corrosion weight loss data (Table 27) showed a highly significant immersion-agent interaction effect. A significant interaction is one which is too large to be explained on the basis of chance and the null hypothesis of no interaction. In the case of a significant interaction the factors are not independent of one another. The simple effects of a factor (such as agent) differ and the magnitude of any simple effect depends upon the level of the other factor (such as immersion) of the interaction term. This can also be stated by saying that the differences in responses to the various treatments (agents) are not of the same order of magnitude from block to block (immersion to immersion). An interaction may mean different things to different people with particular interests and problems. Failure of effects to be additive is the measure of interaction to the statistician. To the chemist an interaction is much the same as reaction. Steel and Torrie (1960) point out that where factors interact, a single factor experiment will lead to disconnected and possibly misleading information.

The fact that the interaction and the differences between immersion over-all means were found to be highly significant was not entirely expected. Both are rather difficult to explain. There are at least four factors which may be involved: (1) Corrosion media, (2) Laboratory exposure conditions, (3) Corrosion products removal, and (4) Metal factors. The first, corrosion media, was the same for each immersion, in that enough solution was prepared for at least five immersions and fresh solution was provided in clean plastic bottles for each immersion. Since solutions of uniform composition were used and the potential effects of the particular agent or agents are the same from immersion-to-immersion this would not seem to be the source of the interaction and immersion variances. The second factor, that of laboratory exposure conditions, was adequately controlled as described in the experimental procedure. The third factor, that of the corrosion products removal process, would not seem to be the source of difficulty either since this was the same after each immersion. The composition of the solution and the process were controlled as well as possible. The data (Table 26) and the analysis of variance results showed that the variation in corrosion from immersion-to-immersion is highly significant. It would seem that since the corrosion media, the laboratory exposure conditions, and the corrosion product removal process were well controlled and uniform from immersion-to-immersion, that the source of variation is primarily related to the metal or metal surface. It is difficult to elaborate on this factor; however it is important and the results show that the amount of corrosion not only varies from immersion-to-immersion, but that the order of immersions as far as corrosiveness varies from agent-to-agent. Analyses of the data did not indicate that the results of a given immersion were dependent upon another immersion's results. It seems that the metal is in some way exhibiting some control over the agents effect from immersion-to-immersion and from agent-to-agent. A study should be conducted in the future to determine if this, some other factor or a combination of factors is the cause of these observed variations. Speller (1951) has pointed out that studies of the process of corrosion in the light of the electrochemical theory have demonstrated that the influence of surface finish and similar external factors may have much more to do with irregular corrosion than any variations in chemical composition or other internal factors. Such effects appear to be primarily responsible for the interaction found. While the immersion over-all means were ranked and tested for significant differences, the results found are not of appreciable practical value in this investigation. For this reason little attention will be given to them in the remainder of these discussions. Likewise, while the agent means were compared for each immersion, it would appear that in view of the role the metal itself may play in the over-all effect of a given agent from immersion-to-immersion, that the agent over-all means averaged over all immersions provides the best estimate of the corrosiveness of a given agent in relation to that of others. Therefore when the corrosiveness of different agents are compared the agent over-all means are used. In certain instances and for certain agents only, the weight loss data from immersion-to-immersion indicates additional information about the general effect of the agents as far as corrosion and these affects are discussed.

There appears to be a decrease in corrosion from immersion 1 to immersion 2 with A_I and A_{II} for each concentration used (except, possibly for the 0.084% concentration of A_I). It would seem that since the main difference here is a previous immersion in the second case and no previous immersion in the first case that perhaps surface effects arising as a result of a previous immersion may have caused the decrease. However, in Table 12 just the reverse effect, namely that of an increase in corrosion was apparent from immersion 1 to 2 with ethylenediaminetetraacetic acid added to 3% sodium hydroxide as compared to the above described decrease with tetrasodium ethylenediaminetetraacetate added to 3% sodium hydroxide. In addition, analyses of the control and the A_{II} data (Table 26) for dependence between immersions by linear correlation coefficient determinations and tests of significance for each possible combination of immersion pairs (10 possible) showed no significant correlations and thus no dependence. The data for A_I, A_{III}, and A_{IV} (Table 26) were tested for dependence between immersion 1 and 2. This data and the above indicated that the outcome of a subsequent immersion is independent of a previous immersion's effects at the 5% probability level. The explanation for the variation in results from immersion-to-immersion with a given agent and for the order of immersion over-all means (Fig. 12) seems to lie in surface, agent, or oxygen availability effects or some combination or interaction of these effects. While the immersion and interaction effects (illustrated in Figures 8, 9, and 10) found throughout these studies are of academic interest, and of secondary interest from a practical standpoint, and since their explanation must be rather general and non-specific as the above, no further time is devoted to them in these discussions.

Statistical analyses of the data showed the following characteristics: (1) The response of a given replicate from immersion-to-immersion is independent of its response in a previous immersion. (2) The response for a subsequent immersion is independent of a previous immersion's effects. (3) When a given response was obtained with a given immersion it was generally uniform over the replicates. (4) The requirement of homogeneity of variance for analyses of variance is satisfied when the distilled water data is analyzed separately from the nine alkaline detergent solutions' data. (5) The same significant differences were found for agent effects and concentration effects whether analyzed together or separately.

The statistical checks described above provide a basis for the fact that the statistical methods employed are sound for the type of data and responses obtained in these studies.

Visual examination results indicated a better over-all condition for A_I, A_{III}, and A_{IV} than for the 3% sodium hydroxide control. The A_{II} on the other hand showed a poorer over-all condition than that of the control.

Temperature effects

Significantly more corrosion was observed at 170°F than at 130°F with each of the three solutions tested. However, in the case of 3% sodium hydroxide plus 0.084% sodium gluconate (A_I) significantly more corrosion was found at 130°F than at 150°F. In addition, the corrosion weight loss difference between 130°F and 150°F, and between 150°F and 170°F was not significant for 3% sodium hydroxide and 3% sodium hydroxide plus 0.156% tetrasodium ethylenediaminetetraacetate (A_{II}), respectively. Arithmetic and Arrhenius plots of the data for each of the three solutions (Figures 14 and 15) did not show a significant linear relationship between corrosion rate and temperature for the respective plots (corrosion rate versus absolute temperature or logarithm of corrosion rate versus the reciprocal of the absolute temperature). The over-all effect of temperature on corrosion is likely the combined effect of temperature on reaction rate, gas solubility, and corrosion products for each of the systems tested. It should be recalled that the results presented in Table 33 consist of the combination of two separate tests' data. The 150°F corrosion weight loss results used here are from a previous test (Table 26), while the 130°F and 170°F corrosion weight loss results are from another test conducted sometime later, but by the same individual. If our attention is centered on the 130°F and 170°F results alone we find a rather definite increase in corrosion rate with increase in temperature for each of the systems tested.

The visual examination results indicated that in general as the temperature increased the over-all appearance and condition of the systems evaluated tended to decrease, but not to a large extent. Thus, general agreement was found between visual examination and weight loss results.

Surface-active agent effect

Addition of a surface-active agent (Triton QS-15) that is recommended for use with alkaline detergent solutions, to improve upon their detergency, did not produce a significant increase or decrease in the corrosivity of a sodium hydroxide-sodium gluconate composition (Table 39). Schwartz, Perry, and Berch (1958) have reviewed studies on the corrosive effects of surface-active agents. They have noted, with regard to representative anionic, cationic, and nonionic agents that their action seems to be specific for individual compounds rather than types. Evans (1960) also concurs with this. It is thus apparent that one should not generalize on the basis of the above findings with regard to the potential effects of other surface-active agents on corrosion.

Length of immersion effect

A common practice is to assess the corrosion which has occurred during an arbitrary period of time, and to adopt the ratio of these two as a representative corrosion rate noting the total time of exposure (Champion (1952)). The purpose in conducting this study was to determine the variation in corrosion weight loss with length of immersion time, since the decision to use a 7 day immersion in all the tests was somewhat arbitrary. Use of one length of exposure, however, allowed standardization and control of the unknown effects of this variable. In addition, the following served as a basis for selecting 7 days as the length of immersion: Preliminary tests seemed to indicate that a 7 day immersion would be satisfactory in producing a reasonable amount of corrosion. It has been recommended that the alkaline wash sections of a washer be emptied, cleaned, and new solution added each operating week. Shaw and McCallion (1959) used a 7 day exposure period in their gluconate-caustic studies, and use of a 7 day exposure in these studies would allow comparison of results. This study on the effect of length of exposure on corrosion was one of the last to be conducted. The reason for this was several delays due to experimental control difficulties. The results of these tests suggest that future research be conducted using 12 hours, 1 day and 2 day exposure periods, except possibly in the case of the sodium hydroxide-tetrasodium ethylenediaminetetraacetate solutions. The reason for little apparent difference in amount of corrosion with 1, 3, 5, and 7 day immersions is probably due to a build up or accumulation of corrosion products which could effectively limit further corrosion. Advantages and disadvantages still remain, however, as to the use of a

1 day or 7 day immersion period. Use of a 1 day immersion period does not itself assure that even its use is best because perhaps an even shorter immersion period might still be better in this respect in some instances. The use of a 7 day immersion period and comparisons based on this, allow any inhibitive or non-inhibitive effects which take place with time, and would occur in practice and have important practical implications to be taken into account in assessing the comparative effects under study. The sodium hydroxide-sodium gluconate solution is significantly more corrosive than the sodium hydroxide solution when the mean for the two immersions' results are compared for either the 1, 3, 5, or 7 day immersions. This is not the case with the sodium hydroxide-tetrasodium ethylenediaminetetraacetate solution, since the amount of corrosion weight loss is significantly greater for a 7 day immersion than for 1, 3, and 5 day immersion periods. So it is evident that in the first case the same results are found no matter what immersion period is used for comparison of effects, while in the second case this is not so, since here a significant increase in corrosion occurs with increased length of immersion. The fact that in one of the three cases a significant increase in corrosion weight loss was found, is itself support for the use of the longer immersion period.

Studies on hard water-sodium hydroxide-sequestering agent systems

The effects of four water softening agents in 3% sodium hydroxide, 12 grain per gallon hard water (consisting of 2/3 as calcium hardness and 1/3 as magnesium hardness) solutions on the corrosion of mild steel were determined. Significantly less corrosion was found with tetrasodium ethylenediaminetetraacetate, A_{II} (33C2), trisodium phosphate, A_{III} (44), and tetrasodium pyrophosphate, A_{IV} (55), than with the 3% sodium hydroxide control (11). The A_{II} (33C2), A_{III} (44), and A_{IV} (55) were, themselves, not significantly different in effect. Significantly more corrosion was found with sodium gluconate, A_{I} (22C2), than with the control. (Numbers given in parentheses are the codes as used in Figure 16 and they denote the use concentrations of the respective agents.)

A comparison of the weight loss data (t test) of the 3% sodium hydroxide, distilled water and hard water controls showed that the 3% sodium hydroxide, hard water control was the significantly more corrosive of the two. The addition of sodium hydroxide to hard water results in the following reactions:

$$Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3\downarrow + Na_2CO_3 + 2H_2O$$

If all the calcium and magnesium ions are complexed, the concentration of sodium carbonate would be the same with A_I, A_{II}, A_{III}, and A_{IV} solutions. In the hard water-sodium hydroxide-sequestering agent systems it is likely the mutual interactions of the several ions present will play a major role in affecting the nature and distribution of corrosion products, and thus, ultimately affect the corrosion rates. It is known for example that hard waters tend to precipitate an insoluble layer (e.g. $CaCO_3$) particularly on the cathodic surfaces of corroding iron (Uhlig (1948)). Such an insoluble layer may contribute to impeding the diffusion of oxygen to the metal in cases where a relatively unprotective layer of corrosion products exists (such as with soft water solutions). On the other hand, such a precipitate may alter an already protective film (such as the ferrous hydroxide film on iron in alkaline solutions) decreasing its over-all protectiveness. It appears that this is the case with the 3% sodium hydroxide, hard water control. The water hardness probably results in alteration of the corrosion product film in such a manner that less resistance is afforded the diffusion of oxygen to the metal. Addition of a water softening agent that will prevent the deposition of an insoluble layer of water hardness compounds on the metal surface then will decrease the corrosion rate found with the 3% sodium hydroxide, hard water control. This appears to occur with A_{II} and A_{IV} which softens by sequestration of the alkaline earth metal cations and with A_{III} which softens by precipitation. The increase in amount of corrosion with A_I may be due to a calcium- or magnesium-gluconate complex existing on the surface of the metal. The metal-gluconate complexes formed, normally considered as solubilized, may exhibit some charge that will allow migration to the cathodes. There they may modify the nature and distribution of corrosion products and perhaps allow more rapid oxygen diffusion to the metal surface, and is so doing promote corrosion. If increasing the concentration of the agent (A_I) tends to more completely sequester the metal-gluconate, thus forming a more stable water soluble complex, more of this complex is then in solution and less on the metal and the corrosion rate is then expected to decrease with increasing concentration of the agent. Concentration effects of A_I and A_{II} are analyzed and discussed in more detail later in this dissertation.

Shaw and McCallion (1959) found more corrosion with 3% sodium hydroxide and 3% sodium hydroxide plus sodium gluconate in their studies than was found in the tests reported in this study. They also reported an increase in corrosion with increase in sodium gluconate concentration which also differs from the results found in this investigation. Several factors differ between these two studies, the most important of which may be the use of rotating specimens in the Shaw and McCallion study. They also employed a test solution volume-to-test specimen surface area-ratio of considerably less than that which is recommended. In addition, only two replicates were used, the results were not analyzed statistically, and the error involved was not measured. The type of metal and corrosion products removal procedures employed by Shaw and McCallion differed from those used in this study. The corrosion products removal procedure employed in their studies was found unsatisfactory for use with mild steel in these studies. The claim (Cooper (1960)) that the use of sodium gluconate results in increased corrosion has been substantiated and the claim (Dvorkovitz and Hawley ($1952_{a,b}$)) of decreased corrosion with its use has been repudiated in these laboratory tests. However, it should be noted that as far as the practical application of these findings, the corrosion aspect due to the use of this agent may be out-weighed by other advantages that may be obtained as a result of its incorporation in cleaning compositions.

The visual examination results indicated a better over-all condition for the A_I, A_{II} and A_{IV} systems than for the A_{III} and the 3% sodium hydroxide control systems (Table 51). The over-all condition of the control, A_I, A_{III}, and A_{IV} systems made with hard water were poorer than that for the same systems made with distilled water. However, with the A_{II} system its over-all condition tended to be poorer with the distilled water solutions than with the hard water solutions. On an over-all basis, more corrosion was found with the 3% sodium hydroxide hard water systems than with the 3% sodium hydroxide distilled water systems, as indicated by both the grand agent over-all mean weight loss and the grand agent over-all visual examination results.

Distilled water and hard water studies combined and compared

Distilled water versus hard water

Results of a test conducted to determine the corrosivity of distilled water and hard water (12 grains per gallon total hardness as calcium carbonate) using the experimental procedures developed for these studies have shown that distilled water is considerably more corrosive (significant, 1% level) than hard water. This finding in itself is not new. However, having corrosion weight loss data for these solutions, determined under the conditions and procedures used throughout the rest of the studies, is advantageous in that more confidence may be attached to comparisons made using these values than to literature values, where experimental conditions may have differed to some extent from those employed here. The corrosion rate found with distilled water of 3.5 MPY (or 135.19 mg/dm^2-week) compares with literature values of 3.1 MPY to 3.5 MPY (Speller (1951) and Uhlig (1948)). This finding itself is important since it reflects favorably upon the experimental methods employed throughout these studies. The difference in corrosivity of the two solutions can be explained as follows: As corrosion proceeds, ferrous hydroxide is formed on the surface of the metal, and due to this and the accompanying increase in pH, calcium carbonate is formed from the calcium bicarbonate in hard water and precipitated on the surface of the metal intermingled with corrosion products. This results in the formation of a less permeable film over the surface of the metal which retards oxygen diffusion. The over-all corrosion rate is decreased in hard water as a result of this retardation of oxygen diffusion to the metal surface. Visual examination results indicated that the appearance of the specimens were slightly poorer in distilled water than in the hard water, while the condition of the distilled water itself was considerably poorer than that of the hard water. The over-all appearance of the two systems was bad with severe corrosion. The visual examination and weight loss data both indicated more corrosion with distilled water than hard water.

Distilled water, distilled water plus tetrasodium ethylenediaminetetraacetate, and hard water corrosion weight loss effects compared

Comparison of the corrosivity of distilled water plus 0.156% tetrasodium ethylenediaminetetraacetate with distilled water and hard water has shown that the former is significantly more corrosive than distilled water and hard water. These results have been explained in a previous section (see the distilled water-sequestering agent section). There are important practical implications that can be drawn from the above findings: (1) The use of tetrasodium ethylenediaminetetraacetate with soft water in the rinse sections of mechanical bottle washing machines could significantly increase corrosion over that normally obtained with soft water alone. (2) An excess of this sequestering agent in washer rinse sections with hard water could also be expected to increase corrosion.

Based on the results in Table 22 phosphates could be used to advantage in corrosion inhibition in the rinse sections of a washer. An excess of phosphate type agent would probably be required in order to both soften the water and to inhibit corrosion. The objections to the use of phosphates which occur when they are used with alkaline solutions at high temperatures are not a great problem in the rinse sections. In the rinse sections of a washer the pH is near neutral and the phosphates are very good sequestrants at this pH. In addition, one of the chief objections to the use of polyphosphates, namely that of reversion to the orthophosphate, which occurs at high temperatures, would not be a serious problem in the rinse sections, since the rinse water is at about room temperature. Sodium gluconate could be used to retard corrosion in rinse sections, but it is not an effective sequestering agent for calcium and magnesium at the pH 7.0 of the rinse sections.

Alkaline detergent, distilled water and hard water studies combined and compared

Caution: The results reported and discussed in this section are presented to indicate trends, and they must be considered as approximate, since results for the two sets of data were pooled even though homogeneity of error variances did not exist for the two sets of data. Analysis of the results (Table 59) in this manner despite the disadvantage noted above allows many comparisons of results that would otherwise not be possible, as shown in Table 60. The marked differences which exist between sodium gluconate in alkaline hard water and distilled water solutions as well as the marked difference between alkaline hard water and distilled water controls are readily apparent. The differences between the alkaline, hard water and alkaline, distilled water trisodium phosphate and tetrasodium pyrophosphate solutions and the tetrasodium ethylenediaminetetraacetate solutions (except at its highest concentration) were found not significant.

The distilled water used in preparing the test solutions made with distilled water was boiled before preparation of the solutions; the hard water was not boiled, since boiling would have induced precipitation of hardness salts. This point in the experimental procedures is important because the oxygen content of the hard water solutions could be expected to be greater than that of the distilled water solutions. The oxygen content in the distilled water solutions at the start of the test was primarily dependent upon the amount of oxygen dissolved from headspace gases during pre-heating of the solutions before adding the test specimens.

Concentration effects of sequestering agents in alkaline distilled water and hard water solutions

The corrosion weight loss of steel specimens in alkaline distilled water solutions containing 0.168% sodium gluconate was significantly greater than that in 0.042% and 0.084%, and between 0.084% and 0.168% sodium gluconate. A plot of corrosion weight loss versus concentration of sodium gluconate gives a straight line of the form

$$\tilde{Y} = 3.065 + 2.601X$$

over the concentration range evaluated. The $\tilde{Y}$ is an estimate of an unknown Y (corrosion weight loss) from a known X (Concentration in percent). The slope of the line (b_{YX}, called the linear regression coefficient of Y on X) and the intercept (a) values being 2.601 and 3.065 respectively, over the concentration range evaluated. Apparently the corrosion weight loss does not follow a linear relationship somewhere between 0.000% and 0.042% sodium gluconate, since the corrosion weight loss found experimentally at 0.000% sodium gluconate was 2.74 mg/dm^2-week. The tendency for corrosion weight loss to increase linearly over the concentration range evaluated (b_{YX} significant at 20% level) can be explained as follows: As the concentration of sequestering agent increases, the potential for more sequestration of corrosion products exists, and as more of the corrosion products which tend to inhibit corrosion in oxygen type corrosion (corrosion products tend to control oxygen diffusion to the cathodes which tends to control corrosion rate) are sequestered, the corrosion rate tends to increase. From a practical standpoint these results would tend to indicate that very heavy excesses of sodium gluconate should be avoided with 3% sodium hydroxide soft water cleaning compositions used for purposes other than softening water (such as detergency).

In alkaline hard water solutions the amount of corrosion decreased as the concentration of sodium gluconate increased. The three possible differences in weight loss as a function of concentration were each significant. A plot of the logarithm of corrosion weight loss versus the reciprocal of sodium gluconate concentration gives a straight line of the form

$$\log \tilde{Y} = 0.7782 + \frac{0.006442}{X}$$

over the concentration range evaluated. The slope (b_{YX}, significant at the 1% level) and intercept (a) values being 0.006442 and 0.7782 respectively. It was anticipated that either one or two mole concentrations of sequestering agent (0.042% or 0.084% sodium gluconate) per mole of alkaline earth metal cations (12 grains per gallon total hardness as calcium carbonate) would result in complete sequestration of the metal cations. Theoretically at least, sequestrant-to-metal mole ratios of less than one, one, and two have been described for sodium gluconate and calcium (Chaberek and Martell (1959)). In practice it is assumed that a mole-to-mole ratio exists and this quantity is then doubled so that commercially 2 moles of sodium gluconate per mole of alkaline earth metal ion are recommended (Shaw and McCallion (1959)). If all the calcium and magnesium ions of the calcium and magnesium carbonates which interfere with the corrosion products' (ferrous hydroxide) normal metal protection were completely sequestered by just sufficient sodium gluconate (such as 0.042%), and thus prevented from becoming intermingled with the corrosion products, a corrosion rate less than that obtained with the 3% sodium hydroxide hard water control (4.13 mg/dm^2-week) and perhaps nearer the 3% sodium hydroxide distilled water control (2.74 mg/dm^2-week) would be expected, but apparently this is not the case, since the test using the mole-to-mole ratio of one (0.042% sodium gluconate) did not produce such an effect. Instead, a very marked increase in corrosion was found. There are at least two approaches to explaining this marked effect, the latter of which seems most reasonable since it can be used more readily to explain the decrease in corrosion with increase in sodium gluconate concentration as well as the marked increase at the lower concentration.

The first approach is to look upon the calcium-gluconate complex formed as an accelerator of corrosion (by a catalytic means for example) where increasing the concentration of the free gluconate from 1 mole (0.042%) to 2 moles (0.084%) to 4 moles (0.168%) tends to increasingly retard the accelerating effect of the calcium-gluconate complex, which is in proportion decreasing in quantity relative to the free gluconate in solution. The second approach to the explanation of the two main effects observed follows: The first of these effects to be explained is the marked increase in corrosion between the control (3% sodium hydroxide, hard water solution) and the lowest sodium gluconate concentration used (where the mole-to-mole ratio was one or 0.042% sodium gluconate). The second effect to be explained is the decrease in corrosion with increase in sodium gluconate concentration from 1 mole to 2 moles to 4 moles of sequestrant per mole of alkaline earth metal cations. The increase in corrosion found between the control and the lower gluconate concentration used may be due to the calcium-gluconate complex being intermingled with the corrosion products and affecting their nature and distribution in such a manner as to ultimately result in increased corrosion. One way this might occur is through incomplete sequestration of the complex or incomplete solubilization and maintaining of the complex in solution. Since at this point we are concerned with a mole-to-mole ratio of one, where each gluconate has a negative charge of one and each metal cation has a positive charge of two, if all the cations and anions combine one-to-one the possibility exists that the calcium- or magnesium-gluconate complex as formed may have a net positive charge, and as such, may act as a molecular-complex cation and be attracted to the cathodes. At the cathodes this complex could modify the nature and distribution of corrosion products in such a manner as to increase the permeability to diffusion of oxygen. If oxygen diffusion is accelerated as a result, then the corrosion rate would be expected to increase to perhaps the extent found. The second effect, namely that of the decreased corrosion with increased sodium gluconate concentration may be due to the formation of a more soluble complex. At the 0.084% concentration there exists two gluconate anions (each having one negative charge) per alkaline earth metal ion (each having a positive charge of two). For this reason there should be many less complexes of some possible net positive charge than in the previous case (0.042% sodium gluconate). The 16% decrease in corrosion from the 1 mole concentration (0.042%) to the 2 mole concentration of gluconate per mole of metal cation, as compared to about a 8% decrease in corrosion from the 2 mole to 4 mole concentration (0.168%), suggests that the sequestrant-to-metal ion ratio may be predominately 2-to-1. The additional decrease in corrosion between the 2 and 4 mole concentration levels could be the result of further improved sequestration. The stability of the 2 mole gluconate-to-1 mole divalent metal cation complexes is probably such that the complexes are continually breaking down and recombining; as the concentration of gluconate is increased from 2 to 4 moles, the chances of recombining are increased, so that at any given time, more stable, water soluble, uncharged complexes are present in solution and free from the metal and its corrosion products. In this manner, as the gluconate concentration increases over the range tested, less calcium-gluconate will be present in the corrosion products and the corrosion products will become a more homogeneous, less permeable oxygen diffusion film and thus corrosion will be retarded.

In the case of some calcium-phosphate complexes their role in corrosion has been explained in a manner somewhat similar to the above. Putilova, Balezin, and Barannik (1960) have reported that the glassy phosphates migrate towards the cathodes in water containing calcium ions and that this differs sharply from the behavior of sodium phosphate dissolved in distilled water where the phosphate ions move towards the anodes. They state that when a calcium salt is present, cathodic migration can take place if positively charged colloidal particles consisting of numerous diphosphate chains joined by calcium atoms are formed. They also point out that the positive charge on the colloidal particles may be due to adsorption of calcium ions by the colloidal calcium phosphate.

Tetrasodium ethylenediaminetetraacetate in alkaline distilled water solutions produced a significant increase in corrosion as the concentration was increased from 1 mole (0.078%) to 4 moles (0.312%) of sequesterant per mole of alkaline earth metal cations. The differences in amount of corrosion between 1 mole (0.078%) and 2 moles (0.156%), and between 2 moles (0.078%) and 4 moles (0.312%) of sequestrant per mole of metal cations were not significant. A plot of the results gives an equation of the form

$$\tilde{Y} = 3.057 + 1.735X$$

where 3.057 is the intercept (a) and 1.735 is the slope or linear regression coefficient (b_{YX}) over the concentration range studied. The linear regression coefficient is significant at the 40% level. The tendency toward some increase in corrosion with increase in concentration that manifests itself in the alkaline distilled water solutions, but not in the alkaline hard water solutions, appears to be due to the same causes as the increase noted with gluconate in alkaline distilled water solutions, despite the fact that tetrasodium ethylenediaminetetraacetate supposedly is not effective in ferrous and ferric ion sequestration above a pH of 12 ("Keys to Chelation" (1959)) which existed in these solutions.

Many instances of corrosion acceleration or retardation due to the use of a variety of sequestering agents under a variety of conditions have been found in these laboratory investigations. A number were unexpected and some were of academic interest. However, from the practical point of view the ultimate decision is whether to use a certain sequestering agent or not under these conditions. This decision can be based upon the laboratory information reported and discussed here, keeping in mind that these were laboratory and not field investigations, and that other advantages (e.g. detergency) to be gained from its incorporation may offset certain corrosion disadvantages. Economically these advantages and disadvantages will need to be weighed against each other in order to facilitate this decision.

SUMMARY AND CONCLUSIONS

Significant acceleration or retardation of the corrosion of mild steel was found with sequestering agents used under a variety of laboratory test conditions similar to those found in practice. The laboratory methods developed specifically for these investigations were responsible for the reliability and reproducibility of results obtained. The percent error of over-all means was generally less than plus or minus 7 percent and a difference of about 10 percent between over-all means was generally significant for samples of 20 replications. Values obtained with the test controls agreed with literature values, and the experimental procedure used was found satisfactory for use by individuals of differing technical training or experience. The corrosion weight loss results were not significantly different for cold rolled and hot rolled AISI No. C 1008 steel specimens immersed in distilled water solutions of alkali, alkali plus gluconate, and alkali plus ethylenediaminetetraacetic acid. Cold rolled steel showed significantly more corrosion in distilled water than hot rolled steel.

Distilled water plus sequestering agents: The corrosivity of distilled water was reduced 97.6 percent with either trisodium phosphate or tetrasodium pyrophosphate (inorganic phosphates) and about 75 percent with sodium gluconate (hydroxycarboxylate). Tetrasodium ethylenediaminetetraacetate (aminopolycarboxylate) caused a 12 percent increase in corrosivity over that found with distilled water.

Distilled water plus sodium hydroxide plus sequestering agents: Three percent sodium hydroxide solutions of tetrasodium ethylenediaminetetraacetate, sodium gluconate, and tetrasodium pyrophosphate listed in order of decreasing corrosivity were each found significantly more corrosive than the control (3 percent sodium hydroxide). Tetrasodium ethylenediaminetetraacetate solution was also more corrosive than the trisodium phosphate solution. The differences in amount of corrosion between the individual agents in group one (tetrasodium ethylenediaminetetraacetate, sodium gluconate, and tetrasodium pyrophosphate), group two (sodium gluconate, tetrasodium pyrophosphate, and trisodium phosphate), and group three (trisodium phosphate and control) were not significant. Distilled water plus trisodium phosphate or tetrasodium pyrophosphate were not significantly more corrosive than sodium hydroxide plus tetrasodium pyrophosphate. Significantly more corrosion was found at 170°F than at 130°F with sodium hydroxide, sodium hydroxide plus sodium gluconate and sodium hydroxide plus tetrasodium ethylenediaminetetraacetate solutions. Corrosivity of sodium hydroxide plus sodium gluconate solutions was not significantly altered by the addition of an amphoteric surface-active agent of the oxyethylated sodium salt type, containing both anionic and cationic centers. Amounts of corrosion found with 3, 5, and 7 day immersion periods (length of specimen exposure) were not significantly greater than that found with the 1 day immersion period of specimens in sodium hydroxide or sodium hydroxide plus sodium gluconate solutions. Significantly more corrosion was found with the 7 day immersion of specimens in sodium hydroxide plus tetrasodium ethylenediaminetetraacetate in their first immersion than with the 1, 3, and 5 day immersions, which were not significantly different.

Hard water plus sodium hydroxide plus sequestering agents: The sodium gluconate solution was much more corrosive than the control, which was significantly more corrosive than tetrasodium pyrophosphate, tetrasodium ethylenediaminetetraacetate, and trisodium phosphate which were themselves not significantly different in corrosivity.

Distilled water and hard water studies combined and compared: Significantly more corrosion was found with distilled water plus tetrasodium ethylenediaminetetraacetate than with distilled water or hard water (12 grains per gallon total hardness as calcium carbonate). Distilled water was significantly more corrosive than hard water. Comparison of the corrosivities of alkaline detergent, distilled water and hard water solutions showed that sodium hydroxide and sodium hydroxide plus sodium gluconate hard water solutions are markedly more corrosive than their distilled water counterparts. Differences in the amount of corrosion found with distilled water and hard water soltuions of trisodium phosphate, tetrasodium pyrophosphate, and tetrasodium ethylenediaminetetraacetate were not significant. Sequestering agent concentration effects were assessed for sodium gluconate and tetrasodium ethylenediaminetetraacetate in sodium hydroxide, distilled water and hard water solutions. Corrosion was found to increase in the distilled water solutions and to decrease in the hard water solutions as the concentration of sodium gluconate increased from 1 mole to 4 moles of sequesterant per mole of alkaline earth metal cations. The predicting equations for sodium gluconate concentration effects on corrosion weight loss with sodium hydroxide, distilled water and hard water solutions over the concentration range evaluated were determined to be

$$\tilde{Y} = 3.065 + 2.601X$$

and

$$\log \tilde{Y} = 0.7782 + \frac{0.006442}{X}$$

respectively. Significantly more corrosion was found at the 4 mole concentration of tetrasodium ethylenediaminetetraacetate than at the 1 mole concentration in the sodium hydroxide, distilled water solutions. Corrosion was not significantly increased or decreased with increase in tetrasodium ethylenediaminetetraacetate concentration in the sodium hydroxide, hard water solutions.

The apparent discrepancy between the effects of sodium gluconate concentration on corrosion in these distilled water and hard water solutions may be explained as follows: In the first case gluconate anions are free to sequester ferrous ions of the ferrous hydroxide protective film of corrosion products, and as the concentration of gluconate is increased more ferrous ions can be sequestered. As the film is diminished in such a manner, less resistance is afforded to the diffusion of oxygen to the cathodes, and corrosion is thereby promoted. In the second case alkaline earth metal cations are present in solution and the gluconate anions would normally be expected to sequester them, thus forming a stable water soluble complex. However, it is suggested that the complex is not adequately solubilized at the lower concentration and that intermingling of this complex with the corrosion products decreases their protectivity and results in increased corrosion. Addition of more gluconate enhances the solubility of the complex leaving less to alter the protective effect of the corrosion products, resulting in less corrosion with increasing gluconate concentration.

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