

Silicate as a Corrosion Inhibitor In Water Systems*

By HENRY L. SHULDENER and SIDNEY SUSSMAN

Introduction

SMALL CONCENTRATIONS of sodium silicate were first added to potable waters during the 1920's. Speller¹ suggested this be done to control corrosion of galvanized steel pipe in domestic water systems. Thresh² in Great Britain first suggested it as a means for minimizing the health hazard resulting from the solution of lead from lead piping, and later as a means for controlling corrosion of ferrous piping.

Speller's suggestion led National Tube Company to sponsor research by Texter at Mellon Institute³ and by Russell at M.I.T.⁴ which demonstrated the effectiveness of sodium silicate in reducing corrosion rates of steel.

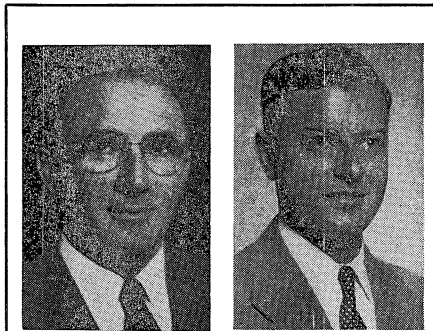
Solid silicate was first used and was applied to the water by means of a drip or by-pass type of feeder.^{4,5} With this type of feeder, silicate addition took place whether or not water was being consumed. High concentrations of dissolved silicate accumulated in the vicinity of the feeder at times of low flow and resulted in the development of difficultly removable silicate deposits which caused partial or complete clogging of the piping. These experiences with deposit formation near the point of application caused silicate treatment of water to acquire a poor reputation.

The early workers^{3,5} also reported that the silicate treatment was effective for only a limited distance from the feeder. Speller placed this limit at 100 to 200 feet of piping.⁶ This conclusion was definitely related to the drip method of feed used initially. The formation of deposits near the point of application depleted silicate available for protection of the piping. Since subsequent developments eliminated this problem, Speller omitted this limitation in later editions of his book.⁵ In fact, later studies at Paignton, England, showed that the silicate was protecting a main at a distance 17 miles from the point of application and throughout the town distribution system.⁷

Despite these early handicaps, the method was soon applied in New York, Boston, Pittsburgh, and Great Britain. The primary goal in these installations was the elimination of "red water" (rusty water) and silicates proved most effective for this purpose.

Speller⁵ at an early date recognized the limitations of solid silicates for water treatment. These materials were virtually insoluble in cold water, thereby limiting the application of the method to hot

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water systems. Speller expressed a hope that a convenient means would be found for the controlled feeding of liquid silicates so as to extend the utility of the method.

This was accomplished five years later by the development of the Chemistat,⁸ a simple, economical, proportional liquid feeding device which finally made possible the use of liquid silicates for corrosion control in both cold and hot water piping systems in buildings without fear of buildup of silicate deposits. Experience with controlled silicate feeding soon showed that it was possible to avoid formation of such undesirable accumulations while permitting the formation of a thin, self-healing, protective film which did not build up on itself. The application of this feeder in buildings, as well as the use of proportionating pumps in the treatment of large municipal water distribution systems, showed that corrosion could be inhibited at very considerable distances

Abstract

The development of a simple, economical proportional liquid feeding device for distributing sodium silicate in domestic water pipes permitted effective and widespread use of this inhibitor. For the past 32 years it has been used for protection of galvanized iron, galvanized steel, yellow brass, and copper water piping in thousands of buildings in East Coast cities which have corrosive water supplies.

Properly controlled, silicate treatment has eliminated rusty water, maintained satisfactory flow rates, and minimized failures due to pitting and to clogging by corrosion products. Comparative field experiments have demonstrated its effectiveness.

Most cases of poor results when using a silicate inhibitor have resulted from improper feeding by dosing methods, piping defects, poor plumbing design or fabrication, or improper operation of the water system, particularly with respect to lack of hot water temperature control.

Studies of the protective mechanism have shown that it involves formation of a thin film containing both silica gel and an absorption compound of silica and the metal hydroxide. Further basic studies are desirable for understanding the respective roles in protective film formation of alkalinity and silica in natural waters as compared to those in added silicate. 5.8.2

from the point at which the silicate was introduced into the piping.

Although the first use of sodium silicate in water systems was directed at eliminating red water or lead pickup and only indirectly at reducing the corrosion of steel, during the intervening years this additive has also been shown to be an effective corrosion inhibitor for galvanized iron, galvanized steel, yellow brass, copper, and aluminum. It is currently being applied for protection of piping in many thousands of residences, apartment buildings, offices, hospitals, laundries, and hotels. Some municipal water distribution systems in Germany, Great Britain, and the United States are silicate-treated for corrosion control. In this country the method is employed for corrosion control in smaller communities, such as Hollywood, Florida; Lebanon, Pennsylvania⁹; Ossining, New York, and many others. Silicates are not used more often for corrosion control in large water systems because of the economic disadvantage when compared to the use of the less expensive lime.

Industrially, sodium silicate is commonly applied as a corrosion inhibitor to protect piping carrying zeolite-softened water, particularly in commercial laundries, and has been added to oil field brines for protection of piping and to water filled gas holders. There is also some use of silicates for corrosion protection of water tanks on shipboard and of the cooling systems of inboard motors on boats.

Theoretical

Conflicting views have been expressed regarding the mechanism by which

sodium silicate minimizes the corrosion in water piping. Early experiences with over-dosing by means of drip feeders led many to believe that the protective layer was a reaction product of the silicate with the hardness of the water and, therefore, that the ultimate buildup of a heavy scale with resultant clogging of pipes must be expected. This view was soon discredited,⁶ although not eliminated in the minds of some people. Even to this day despite the many years of contrary experience since proportional feeding of silicate was introduced, this view in some cases still persists.

Some observers have believed that the major effect of the silicate derived from neutralization of dissolved carbon dioxide by its alkali content. In recent years, investigations by Duffek and McKinney,¹⁰ and by Eliassen and co-workers¹¹ have established that much greater protection is obtained when the pH of a particular environment is adjusted by addition of a silicate, than when it is adjusted to the same final pH by addition of an alkali alone in the absence of any silica.

Fundamental studies by Lehrman and Shuldener^{12, 13} have shown that the protective silica film does not begin to form until there are some corrosion products of the metal present, thus confirming a mechanism suspected many years before by Speller.⁶ The corrosion products form an adsorption compound with silica, removing the latter from solution. Chemical analyses of the protective layer show that it is high in silica. The silica gel-like structure of the film makes it semi-transparent when wet. When dry, it is visible as a thin coating slightly colored, either brown by iron corrosion products or white by zinc corrosion products.

As soon as the thin surface film of adsorption compound forms, further corrosion of the metal surface virtually stops. Because no further corrosion products form, no additional buildup of the film takes place. This mechanism explains why such a film is self-limiting in thickness.

It also explains why the protective film is self-healing when damaged. If the film is removed from a surface by any means, the metal begins to corrode and a fresh surface film forms by reaction with the silica present in the treated water. This, of course, indicates why it is necessary to treat such systems continuously.

Since red water consists of iron oxides in suspension, the fact that the silicate precipitates these in a film on the surface of the piping as fast as formed, explains the great effectiveness of silicate treatment in overcoming red water problems.

Further studies on the mechanism of silicate inhibition are being carried out currently in several laboratories in the United States and Great Britain.

Application

For feeding silicates in large industrial and municipal applications the various types of proportional feed pumps are used.^{7, 14}

The widespread successful application of sodium silicate as a corrosion inhibitor in piping systems of apartment buildings,

office buildings, hotels and similar structures which are characterized by wide fluctuations in the rate of water use and limited maintenance personnel, would have been impossible without the development of a simple hydraulic-type proportional feeder with no moving parts.⁸ This type of feeder, a picture of which is shown in Figure 1, is connected across an orifice inserted in the water line, applying the Venturi principle to feed treatment chemical in proportion to the flow of water.

A cross sectional view of the feeder, shown in Figure 2, indicates how the heavy, viscous sodium silicate solution is present as a separate layer in the lower part of the tank. The water entering the feeder through the inlet impinges upon the water-silicate interface, picking up a small amount of silicate which is carried back into the water line. Tracer studies with a glass hydraulic proportioning feeder and a colored inlet stream show that, following this impingement, the diverted water returns to the top of the tank and flows to the outlet. Thus the silica pickup is independent of the total interface area.

It will be seen from the above description that the amount of silicate solution entering the water line is proportional to the total flow of water so that uniform treatment is maintained under variable flow conditions. When no water is flowing in the line, no treatment chemical enters. The proportioning feeder is always connected below the water line and, therefore, it is impossible for any silicate solution to flow by gravity into the water line.

Because neither inlet nor outlet lines dip into the silicate solution, there can be no pickup of strong chemical from the feeder during any period of low pressure or even negative pressure in the water main. Additional pickup of chemical should there be sudden and heavy reversal of flow in the main is prevented by a baffle inserted just below the outlet line. Independent tests made by the New York City Department of Water Supply, Gas and Electricity demonstrated the correctness of these statements and, as a result, the Department permits installation of this feeder on potable water lines without check valves or vacuum breakers.

In general, it has been found most suitable and economical to utilize the common commercial grade of liquid silicate having a density of 40°–42° Baume and an alkali to silica ratio of 1 Na₂O:3.22 SiO₂. Using this silicate, effective control of red water and of corrosion can be obtained under normal operating conditions by addition of sufficient silicate to increase the silica content of the water by approximately 8 ppm. In some cases it is desirable to increase the initial dosage in order to more rapidly establish a protective film, and in some cases it is possible to reduce the average dosage somewhat and still to maintain the protective film once it has been established.

When applying a chemical to a potable water system, the question of possible overtreatment of the water must be con-

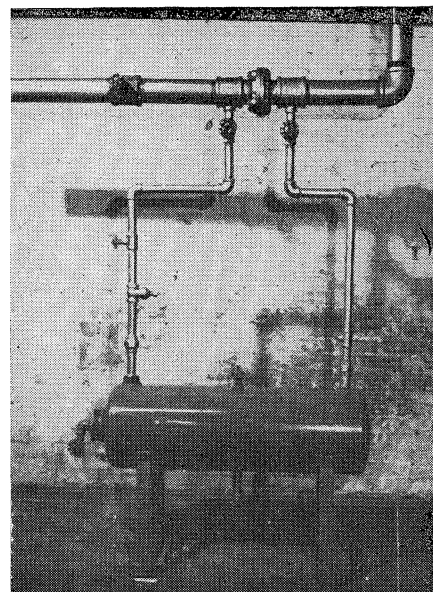


Figure 1—The Chemistat, a hydraulic proportioning feeder, installed across an orifice inserted in a water main for feeding sodium silicate.

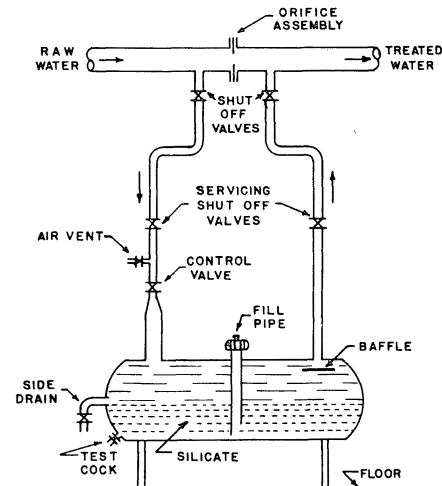


Figure 2—Cross-section of the hydraulic proportioning feeder showing the interface between the treatment chemical and the water layers, and other details of the feeder assembly.

sidered. In New York City,¹⁵ Detroit,¹⁶ and Yonkers, New York, application of chemical treatment to potable waters within buildings is regulated by specific codes, and approval of the chemicals and feeders by the municipal authorities is required.

Field Results

Since 1927 Water Service Laboratories has provided a corrosion control service using sodium silicate as the inhibitor for protection of domestic water piping in large apartment houses, hotels, hospitals, and office buildings in the New York, Philadelphia, and Washington Metropolitan areas. More than 400 large buildings have been treated continuously for more than 10 years and about 50 have been treated continuously for more than 25 years.

Most of the waters being treated are surface supplies, but silicate treatment has also been effective on a number of well supplies which, while much harder

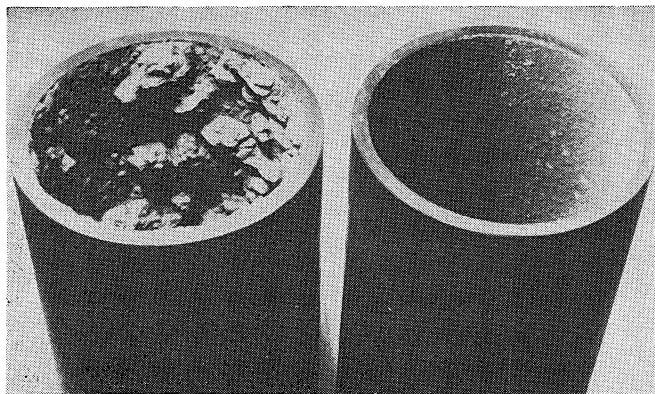


Figure 3—Four inch galvanized iron cold water line from Philadelphia office building. Tuberculated section was in use for two years before silicate treatment of the water was started. The smoother section replaced this when water treatment was started and was in service for an equal length of time.

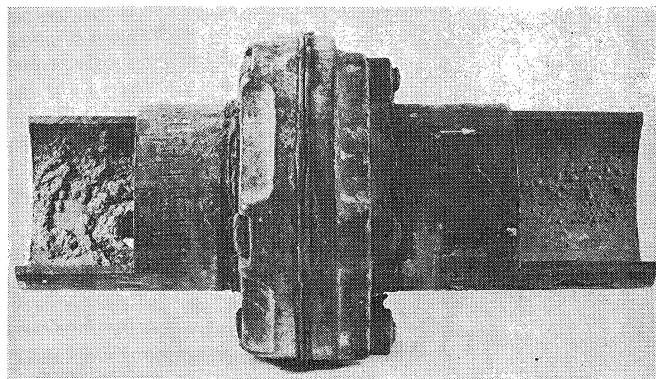


Figure 4—Orifice disc assembly taken from a 15 year old hydraulic proportioning feeder installation in New York City. Note tuberculation of galvanized iron main on the inlet side where no added silicate was present and absence of significant tuberculation on the outlet side where the added silicate entered the water stream.

and containing more natural silica, are aggressive by virtue of their high carbon dioxide content. Table 1 shows some typical analyses of waters being treated.

Several real estate management companies have kept statistical records for a period of years with regard to the development of leaks and to repair costs on groups of buildings using the same water supply. Some of the buildings were being treated with sodium silicate and others were not. These statistical studies have shown that application of silicate treatment is economically justified on the basis of savings in re-plumbing costs. Numerous other case histories have been cited by Stericker¹⁴ of the effectiveness of silicate treatment in minimizing corrosion.

Housing Development Study

Thirty years ago rusty water and poor flow conditions appeared in the galvanized wrought iron hot water system of an apartment house development consisting of 54 large buildings on Long Island. The insurance company which owned and operated this development carried out a comparative test in three adjacent buildings. After installing long test sections of new galvanized iron piping, the water in the first building was not treated, that in the second building was treated with sodium silicate applied by building personnel by means of a drip feeder, and that in the third building was treated by a regular water treatment service by means of a hydraulic proportioning feeder.

Test pieces of the new pipe were removed at yearly intervals and examined by an independent consulting laboratory. After only one year, test pieces from the first two buildings were coated with a thick, rust-colored coating containing about 14 percent iron oxide and were moderately pitted beneath the coating. The test piece from the third building, at which the silica had been proportionately fed by the hydraulic feeder, was coated with a thin tan coating containing only 4 percent iron oxide and beneath which was found only a slight degree of pitting.

After four years the corrosion rate in the piping of the third building was less than 25 percent of that in the piping

TABLE 1—Typical Analyses of Waters Silicate-Treated for Corrosion Control*

PROPERTY	LOCATION AND SOURCE				
	Atlantic City N.J.	New York N.Y. (Catskill)	Philadelphia Pa. (Schuylkill)	Jamaica N.Y.	Idlewild N.Y.
	Surface & Well	Surface	Surface	Well	Well
pH.....	5.5	6.9	6.9	6.8	6.9
Total Hardness (as CaCO ₃)..	13	20	153	308	1650
Calcium (as CaCO ₃)..	6	14	89	124	900
Total Alkalinity (as CaCO ₃)..	6	10	48	218	444
Free Carbon Dioxide (as CO ₂)..	High**	3	12.5	68	100+
Chloride (as Cl) ¹	10	4	23	20	2150
Sulfate (as SO ₄).....	11	8	101	95	350
Silica (as SiO ₂).....	6.5	2.5	8	24.5	30
Total Solids.....	41	31	257	421	4640

* Analyses before treatment. All values, except pH, are in ppm.
** Includes organic acidic materials.

of the other two buildings. At this time serious difficulties became manifest in the hot water piping systems of the many untreated buildings and silicate treatment of the hot water was started in all 54 buildings of the development.

Ten years later, serious flow troubles developed in the untreated cold water lines and silicate treatment was started after substantial piping replacements were made.

Silicate treatment of the hot water permitted the owners to defer total re-piping until the development was twenty-six years old, although at nine years of age, when silicate treatment was started, the hot water piping was in such condition that normal experience in the area indicated that general re-piping would be required within a few years. Thus, the silicate treatment extended the life of this piping from an estimated additional three or four years without treatment to seventeen years with treatment.

AISI Study

An extensive independent field study of the effectiveness of silicate as a corrosion inhibitor was undertaken by the Committee on Steel Pipe Research of the American Iron and Steel Institute.¹⁷ This was done at another large housing development in Brooklyn, New York, which had been built during World War II with galvanized steel piping. Periodic examinations of test specimens removed from both hot and cold water lines in treated and nearby untreated buildings

were made over a period of 17 years. No trouble has been encountered from red water or reduced flow in any of the treated buildings, except for a few short nipples of small diameter supplying kitchen sinks. These difficulties were caused mainly by collected sediment. This was in contrast to normal experience with such pipe carrying New York City water. Rusty water and major pipe replacement in hot water systems are common within five to ten years on this supply.

The tests showed that untreated cold water lines had a greater corrosion rate than treated hot water lines. Over the period of the test, pitting was deeper in the untreated cold water lines than in the treated cold water lines.

Qualitative observations made during this test indicated that some tubercles formed fairly rapidly during the early years, but then tended to flatten out. Similar observations have been reported from silicate-treated municipal water systems in Germany.¹⁸ There is, however, no basis to claims sometimes made that silicate treatment of a water will remove existing rust deposits.

Comparative Pipe Specimens

Figure 3 shows sections of cold water line exposed for two years in a Philadelphia office building. The tuberculated section of this 4 inch pipe had been in use for two years with no water treatment. It was replaced by the other section of pipe at the time that silicate

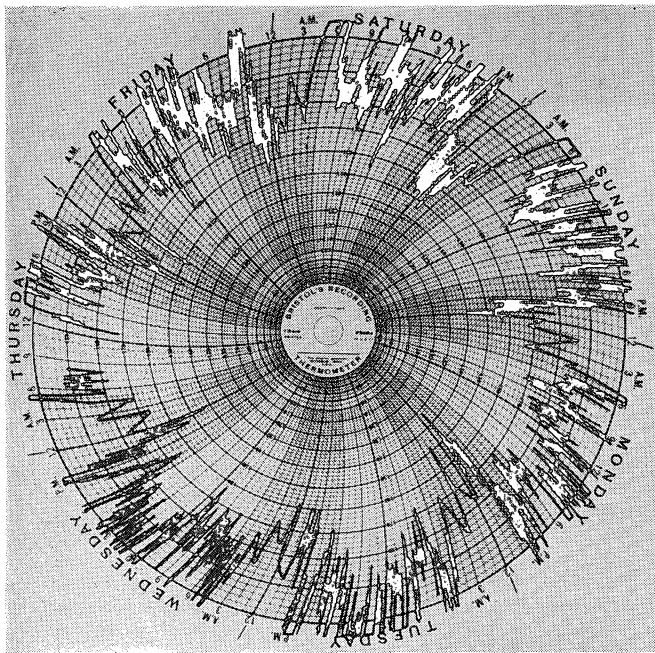


Figure 5—Hot water temperature recorder chart showing poor temperature control at an apartment house. Note the wide and frequent fluctuation, and temperatures as high as 210 F.

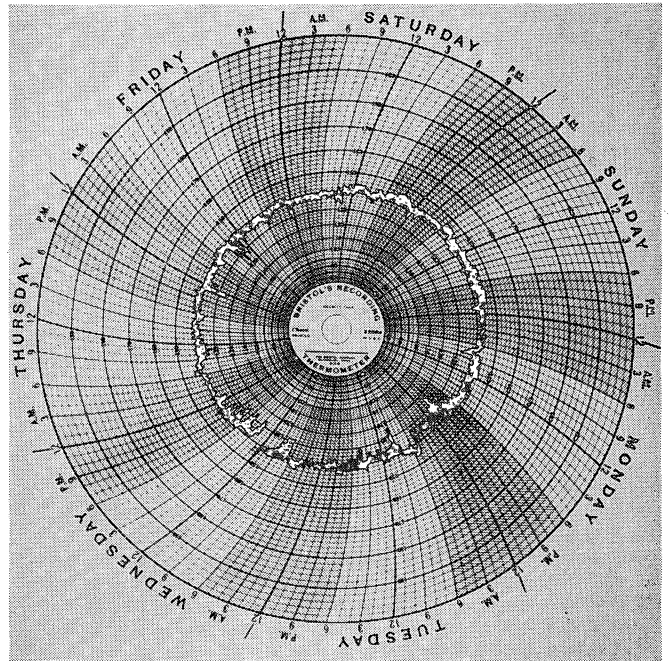


Figure 6—Hot water temperature recorder chart showing very small deviation from 140 F at apartment house with properly adjusted thermostatically controlled mixing valve, and hot water generating and distributing equipment in good working order.

treatment was started and this new section was removed for evaluation after it had been in service for two years. The difference between the tuberculated appearance of the specimen exposed to untreated water and the reasonably smooth coating on the specimen exposed to treated water is made even more apparent by the rust color of the former and the light tan of the latter.

A striking example of the effects of silicate treatment can be seen in Figure 4 which shows an orifice disc which had been in use for 15 years in New York City diverting untreated cold water to the hydraulic proportioning feeder described above. Note the heavy tuberculation of the main at the untreated inlet side and the superficial rust coating at the treated outlet side.

Degree of Protection

Several attempts have been made to evaluate quantitatively the degree of protection afforded to steel pipe by silicate treatment of water. By measurement of the dissolved oxygen content of water entering a test pipe and that of the water leaving the test pipe, Russell⁴ estimated that the corrosion rate was reduced 50 percent in cold water lines and 80 percent in hot water lines by silicate treatment.

On the basis of the iron content of water after passing through a test section of steel pipe, Stericker⁷ estimated that silicate treatment reduced the corrosion rate of steel by 73 percent.

Hudson and Wormwell¹⁹ reported results of a test carried out in the piping system of an English school. Coils of steel wire were cleaned and weighed before and after insertion in sections of the hot water piping system of one building. In the absence of water treatment, corrosion rates in the range 12 to 30 mils per year

were found. When the silica content of the water was increased by 15 ppm, the corrosion rate was reduced to 3.7 mils per year. This corresponds to a reduction of 82 percent in the average corrosion rate of the steel in untreated water, and is a surprisingly good agreement with the above data obtained by other, indirect methods.

Non-Chemical Influences

Poor results obtained with silicate treatment of waters are usually caused by non-chemical factors. These may be related to the original design or construction of the water piping system, to the quality of piping materials, or to operating conditions. This subject has been discussed at some length by Shuldener.²⁰

Typical of poor construction was the case of a hot water storage tank which pitted through at the top within six months because a layer of air was trapped in the upper section as a result of the outlet pipe having been screwed down an inch into the tank instead of being flush with the top.

Poor quality of piping materials is illustrated by the common occurrence of skips, flaws, inclusions, and pinholes in galvanized pipe. These help to localize corrosion when water and temperature conditions are such that potentials of the zinc-iron system are reversed.^{21, 22}

Probably the most important operational factor tending to counteract the protective effects of silicate addition is excessively high hot water temperature. Not only is 140 F a practical water temperature ceiling from the viewpoint of hazards to people, but higher temperatures accelerate the corrosion process, making it increasingly difficult for any given inhibitor dosage to protect metals as temperature rises.

Temperature fluctuations normally as-

sociated with overheating cause expansion and contraction of the piping. This results in leaks at joints due to excessive strains, and flaking off of old rust deposits forming rusty water, developing local stoppages by sedimentation in small diameter branch lines, and accelerating corrosion by exposing fresh metal which behaves anodically. Rusty water thus formed leads users to run large volumes of water to waste in the hope of getting clean water. This can overload the hot water generator and aggravate an already bad operating condition in a continuing vicious cycle. Such temperature fluctuations are shown on a temperature recorder chart from the domestic hot water system of a building in which poor control permitted the hot water to reach 210 F at times (Figure 5). In contrast, Figure 6 shows a temperature recorder chart from a domestic hot water system in which the hot water temperature was thermostatically controlled at about 140 F.

These observations emphasize that silicate treatment of water is not a cure-all and is no substitute for good design, good construction, and good operation of a water piping system.

Summary

Thirty years experience with silicate as a corrosion inhibitor in water systems of large buildings has shown that it provides a simple, safe, and reliable method for eliminating red water and minimizing corrosion in domestic water piping whether it be galvanized, brass, or copper. The experience has also shown that silicate treatment is not a cure-all and cannot be depended upon to overcome the handicaps introduced by poor design, poor construction, or poor operation.

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