

Water Treatment Corrosion ,and Cleaning of Steam Systems

Choice of a water treatment chemistry for steam generators will frequently be a compromise based on the geometry of the particular system and the likelihood of having to cope with periodic contamination of the feedwater.

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It would be impossible to present a complete discussion of all that is involved in the water treatment, corrosion, and chemical cleaning of 1,500 lb./sq. in. steam systems in a short article, and no attempt has been made to do so here. Instead, the purpose of this article is to provide some guidelines for considering the water side aspects of such systems in the hope that these comments will assist in preventing some of the costly damage suffered by 1,500 lb./sq. in. power boilers.

Water Treatment

Make-up preparation – Since the type of primary water treatment equipment employed is a function of raw water quality rather than ultimate use, it will not be discussed here.

The low make-up 1,500 lb./sq. in. utility boiler, generally requiring less than 1% make-up, presents little or no problem in the selection of make-up treatment equipment. A simple two-bed demineralizer or evaporator is usually sufficient. However, high make-up requirements (greater than 10%) present complications. Evaporators are generally too expensive for the production of large quantities of make-up water. It is difficult to economically utilize the large quantity of low level heat given off by such an evaporator. Furthermore, the generation of excessive quantities of carbon dioxide can cause serious condensate line corrosion problems.

All two-bed demineralizer systems produce a certain amount of caustic throw. This is usually in the range of 0.25- to 1.0 parts/million NaOH. In systems where make-up is required in large quantities, this caustic throw usually makes it impossible to control a caustic-free treatment in the steam generating equipment.

A four-bed demineralizer system can be applicable, but this system is fairly expensive and still does not produce top quality water.

For top quality water at nearly the same price as a four-bed demineralizer, a two-bed demineralizer followed by a mixed bed demineralizer usually works out to be the

best choice. A decarbonator installed between the cation and anion units removes most of the carbon dioxide and facilitates operation of the demineralizer plant.

Handling of condensate returns – The following must be taken into account if condensate returns are to be handled properly:

1. Likelihood of periodic contamination.
 - a. Are heat exchangers operated at higher pressures on the process side than on the condensate side?
 - b. Is there a vacuum condenser which uses raw water for cooling?
2. Ability of instrumentation to immediately alarm in the event of contamination.
 - a. Cation conductivity on the condensate works well for ionized solids contamination. Such an instrument records conductivity of a condensate sample after its passage through a column of hydrogen regenerated cation resin. The cation resin removes dissolved gases such as ammonia or morpholine and converts all the salts present to acids. This multiplies the sensitivity of the conductivity reading by approximately 3.5 and eliminates the effect on conductivity by ammoniacal gases. Cation conductivity of a high purity condensate system will generally run substantially less than 0.5 micromhos; readings above 1 micromho should activate an alarm to indicate the need for corrective action.
 - b. Surges of metal oxides are more difficult to instrument, though their occurrence is usually predictable. Unit startup periods and placing of cycle components in-service are the most common times for metal oxide surges to occur.
 3. Ability to take effective corrective action when contamination occurs.
 - a. Overboard the offending stream.
 - b. Large vacuum condensers usually have divided water boxes on the cooling water side. The ability to shut off and drain one of these water boxes permits the isolation of a condenser leak.
 - c. Removal of the unit from service if required. In

many process plants this is not always a practical choice, even if one overlooks the production losses, since sometimes severe damage can be suffered by other plant equipment from loss of steam supply.

The answers to the above questions will determine if simple chemical treatment of the condensate (control of pH and oxygen scavenging) is sufficient or if more sophisticated measures are justified. If uncontrolled contamination is permitted to enter the steam generating equipment, it will almost surely result in deposition on the heat transfer surfaces, corrosion of the steam generator tubing at a rapid rate, or both. If contamination cannot be prevented from entering the main condensate stream, it must then be removed before it gets to the steam generators. This can usually be effectively accomplished with condensate purification equipment. This equipment includes some form of ion exchange equipment plus filtration of particulate matter.

Condensate polishing systems – The most commonly employed form of condensate polishing equipment used in process plants is the sodium regenerated cation unit. It usually uses a resin bed 3 ft. deep and operates at a flow rate between 25- and 50 gal./min./ft.² of bed area. Such a system has numerous advantages. It removes all hardness (calcium and magnesium) and will tend to neutralize mineral acid. It will also remove 60- to 90% of suspended iron oxides by in-depth filtration. It can be operated at temperatures to at least 300°F. It is inexpensive in capital cost and in terms of operating expense. This system also has some disadvantages. It will not remove cations other than hardness and will remove no anions, of which silica, in particular, may create a problem. During the time when the system is processing contaminated condensate, it will usually result in the formation of some free caustic in the steam generator as a result of forming sodium carbonate in the condensate. Although this caustic formation is undesirable, for reasons elaborated on later in this article, it can usually be controlled by careful feed of acid phosphates to the steam generator.

Another system of condensate polishing equipment is the use of powdered resins on a supporting cartridge. This system utilizes various ratios of powdered cation and anion resin in a mixed form. The advantages of this system are that it provides an excellent filter for particulate matter, it removes both cations and anions, and it can be operated at fairly high temperatures.

There are also some disadvantages. Its ion exchange capacity above 200°F is very poor because the anion resin does not perform well at these high temperatures. Replacement resin costs can be very high when frequent contamination is experienced. The resin is not regenerated and is thrown away after it is depleted. For this reason, the quantities of resin used in each charge are small and, because of this, there is a very limited ion exchange capacity in the event of gross contamination.

The most commonly used condensate purification system in high pressure utility plants is a deep bed system of mixed cation and anion resins. This system employs a 3 ft. deep bed using a 2:1 cation to anion resin ratio and operates at flow rates between 25- and 50 gal./min./ft.²

The advantages of this system are as follows: It produces very high purity water in terms of ionized salts. It is also capable of removing 60- to 90% of the iron oxides by in-depth filtration. It can handle fairly heavy loads of contamination for long periods. Regeneration and resin replacement costs are usually not excessive.

There are also some disadvantages. The system cannot be operated at temperatures much above 130°F because of anion resin degradation. Regeneration costs can be high if the cation resin is operated in the hydrogen form and a high cycle pH is maintained. The installed cost is the highest of the three listed systems. It is also the most complicated to operate and requires more building space.

Chemical Treatment

The heat transfer rates encountered in the steam generating equipment of a synthetic ammonia plant are lower than those in a fossil fuel fired 1,500 lb./sq. in. utility or paper mill boiler. However, it is the writer's opinion that because of the physical geometry of some parts of the steam generators in the ammonia plant, they are probably more vulnerable to internal deposit build-up and corrosion than most conventional 1,500 lb./sq. in. boilers. Therefore, we should make every effort to use a chemical treatment which minimizes corrosion even under adverse conditions.

The principle objectives of internal boiler water treatment are:

1. It should not adversely affect steam purity.
2. It should maintain an alkaline condition with some reserve for an acid feedwater upset if this is a periodic likelihood.
3. It should reduce the insulating effect of boiler deposits if and when hardness inleakage should occur.
4. The treatment should, in itself, be non-corrosive.

It would be well at this point to examine the various boiler water treatment additives from the standpoint of their corrosivity. It is apparent from Figure 1 that potassium hydroxide, potassium phosphate, and sodium hydroxide (three commonly used boiler water treatments) can be extremely corrosive to carbon steel when concentrated. However, sodium phosphate and lithium

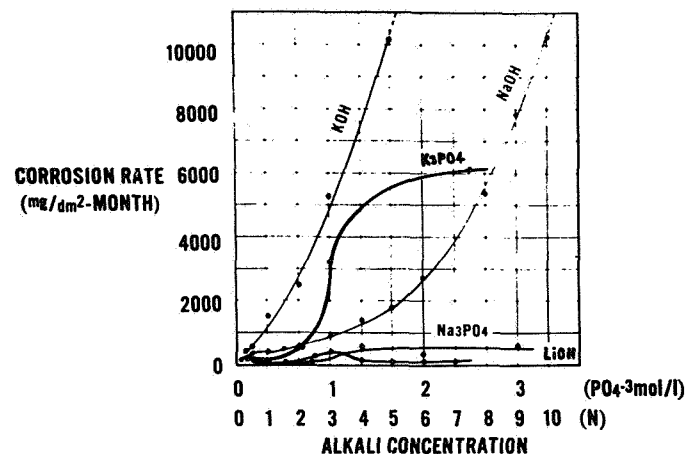


Figure 1. The corrosivity of various boiler water treatment additives.

hydroxide show little tendency to produce accelerated corrosion. Lithium hydroxide is rarely used as a boiler water treatment because of expense. Sodium phosphate is by far the most popular solid chemical treatment used in high pressure boilers today. Many people complain about sodium phosphate because of its tendency to "hide-out" at the higher operating pressures. Actually, this is a blessing in disguise. The reason that sodium phosphate does not show great corrosivity under concentrated conditions is because, before it reaches a concentration at which it is highly corrosive, it comes out of solution.

I would like to emphasize at this point that pure water is not corrosive in an operating boiler. However, it must be truly pure, and it must be maintained in this pure condition. If your plant is operating with mixed bed demineralized make-up and mixed bed demineralized condensate polishing, or there is no possibility of condensate contamination, then volatile treatment using no solid additives is probably the best. There are many years of operating experience with once-through boilers operated with this type of treatment. We have never experienced an incident of in-service internal corrosion on any of our once-through boilers in this country. They all have condensate polishing.

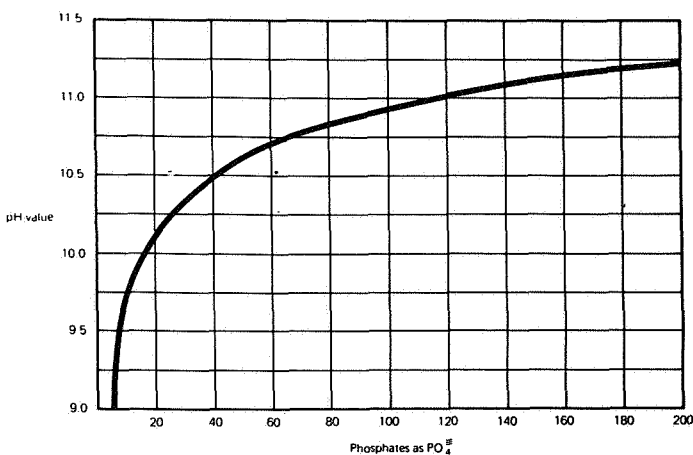


Figure 2. Approximate pH values of trisodium phosphate solutions.

However, if periodic feedwater contamination is a possibility, some form of coordinated phosphate treatment (using sodium phosphate) is by far the best choice. Figure 2 shows the coordinated phosphate-pH curve which is commonly used to control coordinated phosphate treatment. A mixture of phosphates is fed to the boiler so as to maintain the boiler water pH at a point slightly below the curve. In this way no free caustic should exist.

If the pH-phosphate relationship falls above the curve, indicating free sodium hydroxide, the addition of monosodium or disodium phosphate will react with the free caustic to bring the point back beneath the curve. In 1,500 lb./sq. in. power boilers operating on coordinated phosphate treatment it is common to carry a phosphate concentration between 20 and 30 parts/million which will provide a boiler water pH range between 10.1 and 10.3

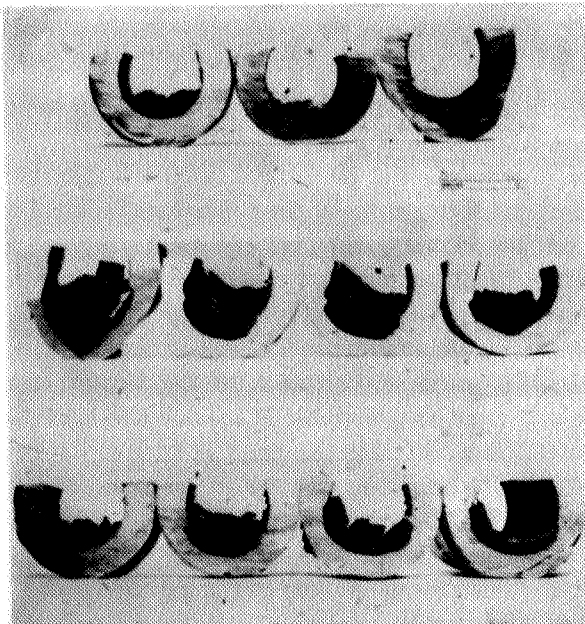


Figure 3. The effect of strong alkali attack on a boiler tube.

Corrosion

In the literal sense, corrosion is always taking place within a steam generator when it is in service, but at such a low rate that it does not affect the useful life of the equipment.

The following discussion on internal corrosion of steam generating equipment deals only with concentrated cell corrosion which can destroy a new boiler tube in a matter of hours. In-service dissolved oxygen attack, which usually affects heaters and economizers and is rarely a problem in high pressure boilers, will not be considered here.

Strong alkali attack — As noted, Figure 1, strong alkalis (potassium hydroxide, potassium phosphate, and sodium hydroxide) exhibit high corrosion rates on carbon steel when they are concentrated. Figure 3 demonstrates the effect of this attack in an operating boiler tube. This tube was destroyed in approximately 30 hr. at our Alliance Research Center's heat transfer test facility. Water entering this test tube contained only 25 parts/million of free sodium hydroxide. However, this quantity of sodium hydroxide can be concentrated by the boiling process to levels approaching 10% or greater. When this occurs, the caustic reacts with the protective magnitite on the internal tube surface. This reaction destroys the protective magnitite and exposes the bare steel surface to further reaction with water. This produces additional magnitite which, in turn, is destroyed and reformed. The result of this series of reactions is gross transgranular gouging of the tube metal and the deposition of huge quantities of magnitite in the tube.

It is clear that considerable risk is involved with the use of strong alkalis in the treatment of high pressure boilers. The role of sodium phosphate in boiler corrosion is somewhat less clear. As indicated in Figure 2, if chemical control is maintained below the coordinated phosphate-pH curve, theoretically no free sodium hydroxide should exist.

However, some theories contend that when trisodium phosphate concentrates to a level where precipitation occurs, the precipitation takes place in a form providing a 2.6:1 ratio of sodium to phosphate. Thus, it is contended that a control ratio of 2.6:1 sodium to phosphate should be carried in the boiler water to prevent the formation of free caustic under adverse conditions.

There are still other factors to be considered, however. Magnetic iron oxide demonstrates some anion exchange properties. We have introduced a solution of Na_3PO_4 through a column of magnetite and found less phosphate in the effluent than in the influent and a higher pH in the effluent plus some free sodium hydroxide. We have also found sodium iron phosphate in heavy magnetite deposits in boiler tube corrosion failures. Thus, it would seem that heavy magnetite deposits in a heat absorbing zone of a steam generator and, in the presence of Na_3PO_4 , will produce NaFePO_4 plus free NaOH . If this free NaOH is sufficiently concentrated, it will produce tube metal corrosion. Such a condition is unlikely to occur unless a heavy magnetite deposit is present or unless a condition of steam blanketing exists.

Hydrogen damage – This type of corrosion occurs when hydrogen (probably in atomic form) enters carbon steel at the grain boundaries. Under favorable temperature and pressure conditions, the hydrogen will react with the carbon to form methane. Since the methane molecule is very large in comparison to the volume previously occupied by the carbon hydrogen atoms, it exerts tremendous internal pressures between the grains of the steel. These pressures are sufficient to burst the grains apart, causing fissures in the structure. The physical evidence of hydrogen damage is a myriad of micro fissures accompanied by partial or total decarboration of the steel in the area of the fissures. Hydrogen damage of boiler tubing is a secondary form of corrosion resulting from hydrogen produced by a primary corrosion mechanism. A hard brittle overlay is always found where hydrogen damage has occurred. This overlay is essential to retard the escape of hydrogen from the metal surface to the boiler water. A corrosive contaminate is required to produce hydrogen damage in boiler tubing within time periods of several thousand hours or less. Experience with hydrogen damage in operating boilers has usually been associated with the presence of a mineral acid condition in the boiler water.

Figure 4 shows a tube from a 1,500 lb./sq. in boiler which has failed from hydrogen damage. Note the extreme fissuring of the tube. A minimal amount of metal loss usually accompanies hydrogen damage.

In the early 1960's we operated a test loop in a power plant for the purpose of producing hydrogen damage under controlled conditions. Figure 5 shows the test tube failure from hydrogen damage experienced during one of the test runs. This tube failed in 59 hr. It was operated on volatile treatment (zero solids) with a contaminate feed of 0.6 parts/million magnesium chloride.

It should be noted that volatile treatment offers no protection against the influx of a mineral acid forming contaminate. At saturation temperature of a high pressure



Figure 4. Boiler tube failure due to hydrogen damage attack.

boiler the ammonia present is almost totally associated and virtually no NH_4^+ ions or OH^- ions exist.

It has also been observed that volatile treated boilers (except those which have full flow condensate polishing) have experienced a much higher incidence of hydrogen damage than solids treated boilers.

Sodium phosphate does provide limited protection against the influence of mineral acids to the boiler. Figure 6 shows another test tube from the hydrogen damage test facility. In this test run the boiler water was treated with 5 parts/million phosphate and the same 0.6 parts/million magnesium chloride feed was maintained as in the previous test. This tube lasted 2,500 hr. before failure (which was caused by overheating). A small area of hydrogen damaged metal was found in the tube. This was approximately 1 in. dia. and the tube did not fail at this location.

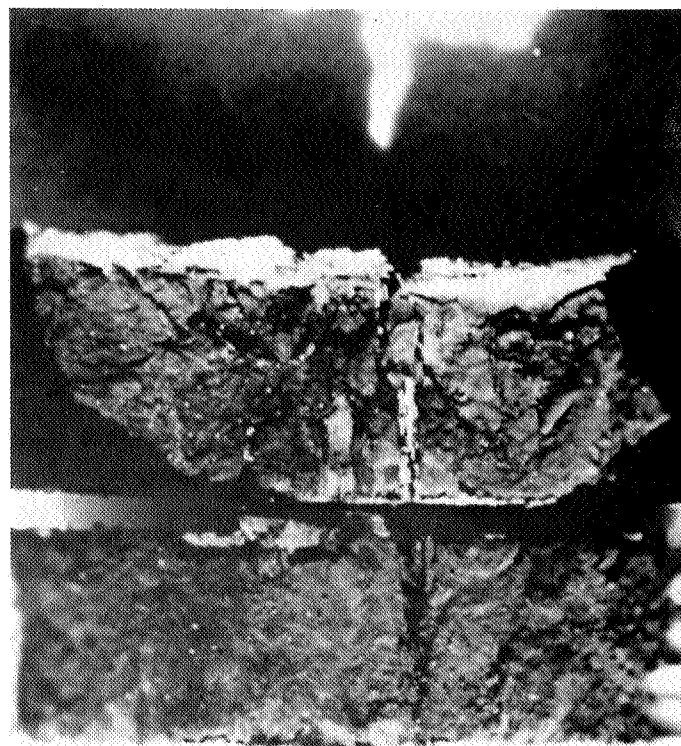


Figure 5. Bent section of hydrogen damage test specimen (showing hard overlay).



Figure 6. Hydrogen damage test specimen which was treated with sodium phosphate.

From the proceeding discussion it might be concluded that there is no totally safe and perfect boiler water treatment. This is certainly true; there is rarely a perfect solution to any problem.

Chemical Cleaning

Maintaining clean heat transfer surfaces offers a partial solution to problems of both corrosion and overheat due to impairment of heat transfer. It was clearly established in the ASME Corrosion Research Program that an internally fouled tube is tremendously more vulnerable to corrosion from a chemical upset than is a clean tube. Field experience in high pressure power plants substantiates these findings.

The degree of internal fouling required to create problems varies with heat transfer rates and water chemistry conditions. Many people in the power industry equate the magnitude of internal tube deposits in terms of gm./ft.² of deposit (mechanically removed by scraping) from a given area.

Experience and testing indicates that the quantity of normal boiler tube deposit (metal oxides and hardness sludge) of the porous type required to produce a significant tube metal temperature elevation at high heat absorption rates is about 20 gm./ft.². However, less than half this quantity may be sufficient to trap boiler water and concentrate boiler water solids (such as strong alkalies) to a

dangerously corrosive level. Thus, it can be seen that whenever it is possible to operate the steam generators so as to totally eliminate all potentially corrosive boiler water solids, a greater latitude in internal cleanliness can be safely tolerated.

Regardless, it must be accepted that, eventually, internal fouling of the heat transfer surfaces will reach a point where chemical cleaning of the steam generators is required if safe and reliable operation of the system is to continue. The reasons for this are many, and space does not permit a discussion of them here, but, experience in the power industry certainly substantiates this position.

The required frequency of chemical cleanings will vary with plant design and operating conditions. I do not have sufficient personal experience with operating 1,500 lb./sq. in. ammonia plant steam systems to predict this frequency, but I would estimate that chemical cleaning every five years is normal for 1,500 lb./sq. in. power boilers.

The most common procedure for chemical cleaning of 1,500 lb./sq. in power boilers is the fill-and-soak method using a 5% HCl solution. Copper can be removed by an ammonium-bromate rinse preceding the acid soak, or by using a copper complexing agent along with the HCl. This procedure is effective and quite safe where all components of the system are drainable. However, in a few cases acid has been permitted to remain in the system and enter the boiler upon its return to service. This usually results in gross hydrogen damage to the unit and a long and costly repair.

Nondrainable surfaces substantially increase the potential for leaving acid in the system, and for this reason I am very reluctant to employ mineral acids to clean nondrainable surfaces except as a last resort.

The nondrainable bayonette heat exchanger usually present in 1,500 lb./sq. in, ammonia plant steam systems should lead one to consider other solvents for chemical cleaning of this equipment. Organic solvents are a logical choice for many such cleaning problems. Their decomposition temperature is sufficiently low that, should some be left in the system, it will likely decompose to harmless gases before any extensive damage to the equipment occurs.

An organic acid mixture which has experienced much success in cleaning once-through boilers and nondrainable superheaters and reheaters is one consisting of 2% hydroxyacetic acid, 1% formic acid, 0.3% ammonium-bifluoride, and inhibitor. It is essential that the mixture be circulated to achieve effective cleaning. Velocities in the range of 1- to 4 ft./sec. at a temperature of 200°F are generally employed. Cleaning periods range from 4- to 6 hr. After displacement of the solvent with demineralized water, a passivation with 500 parts/million and 10 parts/million ammonia at 200°F for 2 hr. completes the cleaning procedure.

We have successfully cleaned numerous nondrainable superheaters and reheaters using this method. Although strong efforts are made to assure that all solvents have been removed from the system, there have been a few instances when some remained when the unit returned to service. Fortunately, because of the low decomposition temperature of this solvent, no serious consequences resulted.

Where deposits have been particularly heavy, increasing the organic acid strength and contact time have usually been effective in removing them.

Various procedures employing formulations of EDTA have also been effective in safely cleaning equipment of the type described above.

It is very worthwhile to remove a tube sample from the equipment to be cleaned prior to the cleaning. Thus, a deposit analysis can be performed and an effective procedure developed in the laboratory. This maximizes the likelihood of a successful cleaning in the field. As with most endeavors, the success of chemical cleaning is largely dependent on the care that is put into the planning and performance.

Summary

1. Steam systems operating at 1,500 lb./sq. in. require high purity make-up and consistently uncontaminated condensate returns.

2. Choice of a water treatment chemistry for the steam generators will frequently be a compromise based on geometry of the particular system and the likelihood of having to cope with periodic contamination of the feedwater.

3. Steam systems at 1,500 lb./sq. in. are susceptible to the same types of accelerated corrosion mechanisms that are experienced at the higher operating pressures.

4. Periodic chemical cleaning of the steam generators must be considered inevitable.

a. Mineral acids entail considerable risk when used to clean nondrainable surfaces

b. Organic solvents are usually a safer choice for such geometry. #

DISCUSSION

D.E. CLAPPER, American Cyanamid Co: Most Ammonia Plant operators have been faced with some synthesis gas leaks going into boiler feedwater at defective heat exchangers; bringing hydrogen, ammonia, and nitrogen and other components in the synthesis gas loop into the 1500 pound boiler system. In your experience, have you had any occasion to predict what would occur in a boiler system under these circumstances with perhaps as much as 50 parts per million ammonia showing up in the boiler steam.

LUX: Ammonia will not hurt the steam generating equipment. Any detrimental effects from high ammonia levels will be in the condensing part of your system. If you have copper alloys, and you have a significant amount of oxygen present, you can get very serious copper attack. But as far as the steam generator is concerned, ammonia has no adverse effect on it. One reason for this is that, at the temperature at which the steam generator is operating, the ammonia is totally associated. You have virtually no OH-ions and no NH_4^+ ions.

This is also the reason that, on volatile treatment using ammonia, you cannot consider that the ammonia is any protection against a mineral acid condition. If you have boiler water contamination from magnesium chloride or a similar salt forming hydrochloric acid, you will find no difference in hydrogen evolution (which is a good measure of corrosion rate) regardless of how much ammonia you feed to the system because the ammonia is totally associated and does nothing for you.



LUX, J.A.