STEAM GENERATION IN ORGANIC FOOD PROCESSING SYSTEMS

Background Paper for the Petitions for Ammonium Hydroxide, Cyclohexylamine, Diethylaminoethanol Morpholine, and Octadecylamine

Background

Live steam is used to process a large number of foods, including many products that are sold as 'certified organic.' Equipment to generate steam and use it for industrial purposes has existed since at least the middle of the 18th Century (Britannica, 2001). Efficient use of steam to prepare food beyond household scale was documented by the early 19th century (Giedion, 1948). While fuels, metallurgy, control systems, and maintenance programs have changed since that time, the fundamental scientific principles, basic designs, and problems associated with those systems have remained constant. The production of superheated water under pressure suitable for direct food contact— known as 'culinary steam'— requires food-grade equipment, clean water, and sanitary conditions where food contact is a possibility. Food processors have fewer options in metals, water treatments, fuels, and other aspects of steam generation and boiler operations than those who operate boilers for non-food uses, such as electric power generation.

Organic food processors face even stricter requirements than those of non-organic food processors. Because water is a non-organic ingredient, it is not subject to the same requirements as organic ingredients. Unlike any other non-organic ingredient except salt, water may exceed 5% of the weight of a processed product labeled 'organic' and '100% organic' [7 USC 6510(a)(4), and 7 CFR 205.301(b) and 7 CFR 205.301(a)].

Water used in organic processing must meet two basic requirements.

(1) The Organic Foods Production Act [7 USC 6510(a)(7)] requires that water used in processing meet Safe Drinking Water Act (SDWA) standards [42 USC 300(f) *et seq.*]. If there is unavoidable residual environmental contamination beyond the control of the processor, contaminants in the water cannot exceed the Maximum Contamination Limits (MCLs) established by the SDWA. This is assumed to include water in all of its phases: liquid water is used as an ingredient and processing aid for many operations; ice is used to remove field heat and prevent spoilage of produce; and live steam used in direct food contact for a variety of processes.

(2) Processing aids used to treat water all fall under the definition of processing aids in 7 CFR 205.2. This states: "a substance that is added to a food for its technical of functional effect in the processing but is present in the finished food at insignificant levels and does not have any technical or functional effect in that food." Such processing aids must either be organically produced or be on the National List. Otherwise, they are prohibited for contact with foods labeled organic (95% organic ingredients) and ingredients represented to be organically produced (7 CFR 205.301).

Therefore, steam purity is of concern to comply with organic standards. Ideal steam is 100% vaporized water. Liquid water, as well as solid, liquid, and vapor chemical contaminants degrade steam purity. These impurities are collectively known as 'carryover.' Carryover is generally classified as either mechanical or vaporous (chemical) (Bellows, 1997). Mechanical carryover occurs from high levels of solids in the water and equipment malfunctions. Vaporous or chemical carryover is the contamination of steam by water-soluble chemicals. Water treatment can help water meet organic standards, but chemical treatments may also jeopardize organic integrity. To understand how water treatments fit in organic standards, it is helpful to have an understanding of why and how these chemicals are used.

This Technical Advisory Panel (TAP) review is based on the information available as of the date of this review. The information and advice presented to the NOSB is based on a technical evaluation is not intended to incorporate commercial availability, socio-economic impact, or any other factor that the NOSB and the USDA may want to consider in making their decisions.

Conditions Requiring Water Treatment

Typical problems that occur with steam equipment are pitting, deposition of insoluble compounds (scale), and corrosion. This damage is mitigated through system design, selection of suitable fabrication materials, process control, and the use of controlled dosages of particular substances that prevent or reduce these problems (Kohan, 1997).

Pitting is generally caused by the impact of solids against the sides of a boiler. The best solution for this is the filtration of water to remove such solids (Kohan, 1997). Some filters may use chelating agents to attract and retain solids through chemical reaction. Scale is a coating of thermally non-conducting solids on the waterside of a boiler, usually composed mainly of precipitated calcium carbonate ($CaCO_3$). This frequently is the result of water that has a high mineral content, known as 'hard' water.

Water can be treated a number of ways before being fed into a boiler to remove calcium and other minerals responsible for scaling. Filtration, activated carbon, ion exchange, and reverse osmosis (RO) are all used by food processors to remove undesirable particles and chemicals from water. The NOSB has not addressed ion exchange for organic ingredients. Water can be deionized by filtration with either natural or synthetic substances (Helfferich, 1962). The use of synthetic resins as processing aids would appear to prohibit their direct contact with organic ingredients. However, the use of ion exchange has been reviewed by the NOSB to produce other non-organic ingredients that appear on the National List, e.g. enzymes. Pretreatment of water with ion exchange does not appear to leave any residues of incidental ingredients that would compromise organic integrity. Various colloids and chelating agents can also remove minerals from feedwater.

Water may also be chemically treated to prevent scale. Some of these are on the National List, but may not be annotated for certain uses. Among these are sodium phosphates, lignin sulfonates, sodium hydroxide, and sodium silicate. These compounds can usually be reduced to acceptable levels by precipitation (Jackson, 1987), filters, or traps. Therefore, scale treatment has generally not been considered a problem for either organic processors or certifiers. However, the chemicals used to inhibit corrosion are a significant challenge for the organic industry.

Corrosion: Causes and Prevention

Most of this discussion, and the subsequent TAP reviews, will focus on corrosion and its management. Corrosion is the wear, breach, and ultimate failure of the vessel that contains the water. Corrosion will not occur in a boiler that has pure water from which all the air has been removed (Ward, 1936). Similarly, because it is a vapor and is uncontaminated by corrosive salts, steam by itself is not corrosive to stainless steel (APV Crepaco, 2000). Because food is not produced in a perfect world, these conditions never exist in a food processing facility. While corrosion can never be eliminated, various steps can be taken to reduce it. Corrosion inhibitors offer only one method of corrosion control (Nathan, 1965). A number of forms of corrosion are not chemically treated, and is addressed through design, manufacturing, and physical maintenance (Basu, Kefa, and Jestin, 2000).

Amine-type boiler additives are used to protect steam lines and condensate systems from metal loss caused by oxygen and carbon dioxide corrosion. Corrosion results as the product of the following chemical reactions (Betz, 1980):

1. $Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$
2. $Fe(OH)_3 \rightarrow Fe^{++} + 2OH^- \rightarrow Fe_2O_3 + 3H_2O$
3. $4Fe + 6H_2O + 3O_2 \rightarrow Fe(OH)_3$

Therefore iron (steel) can corrode forming ferric oxide (rust) in boiler systems and condensate lines. A further mechanism of corrosion of boiler systems is from dissolved carbon dioxide in the water to form carbonic acid. As carbon dioxide dissolves in the water, it causes the pH to be depressed by increasing the hydrogen ion concentration according to the reaction:

4. $CO_2 + H_2O \rightarrow H_2CO_3$

The hydrogen from carbonic acid reacts with iron to form ferrous bicarbonate according to the following equation:

5. $2H_2CO_3 + Fe \rightarrow Fe(HCO_3)_2 + H_2$

Carbon dioxide enters the system either as a dissolved gas or combined in alkaline components of water hardness— bicarbonate or carbonate— alkalinity of the boiler feed water. Dissolved carbon dioxide will be removed from the feedwater by a properly operated deaerating heater, but the combined carbon dioxide will remain in the feedwater. The potential for carbon dioxide corrosion in a condensate system can be reduced by lowering the alkalinity of the boiler feed water by various external treatment methods such as water softening, ion exchange, or reverse osmosis (Betz, 1980).

Additionally, oxygen can enter the boiler and condensate by direct absorption of air and by introduction with the feed water and subsequent flashing over with the steam. Depending on the plant and operations, either source could predominate. With proper mechanical deaeration and chemical oxygen scavenging all oxygen can be eliminated from boiler feed water. Good system design can minimize air contact with the condensate and subsequent oxygen absorption.

A number of chemical additives are used to treat boiler water to reduce certain production problems related to the operation of boilers. A list of FDA approved additives is contained in Appendix 1. Several of these items have already been reviewed by the TAP, recommended by the NOSB, and listed by the NOP for use in organic food processing. These include citric acid, potassium hydroxide, and sodium hydroxide. Some are listed, but do not have annotations that do not include boiler water additives, for example lignosulfonic acid.

Boiler Additives

In addition to these various approaches to reduce corrosion, most operating boiler systems use various compounds to treat or concentrate boiler water, either in the infeed water lines or in the boiler. Some of these are added to the infeed raw water; others are injected into the boiler; another use is with condensate return water. Most chemically treated corrosion can be classified according to the chemical reaction that causes it as either *acid* corrosion or *oxygen* corrosion (Kohan, 1997). *Caustic* corrosion is also a factor in a number of systems (Bradford, 1993; Basu, Kefa, and Jestin, 2000).

Acid corrosion, as the name implies, is the eating of the surface by a solution that has a pH below neutral. Various acids are responsible for this, depending on the water source. The identification and removal of the source of the acid or the addition of an alkali or caustic substance to raise the pH are the standard approaches. These function by raising the pH of the boiler water. Four commonly used substances used for such purposes are on the National List: sodium carbonate or soda ash (Na_2CO_3); sodium hydroxide, lye or caustic soda ($NaOH$); sodium bicarbonate ($NaHCO_3$); and potassium hydroxide (KOH). A fifth— ammonium hydroxide (NH_4OH)— is being petitioned. Caustic corrosion will often occur as a result of the use of these substances, and is often solved simply by discontinuing their use (Bradford, 1993).

Free oxygen (O_2) present in water is the cause of oxygen corrosion. Oxygen can either react directly with the boiler metal and cause pitting, or it can serve as a catalyst with other elements in the water that corrode the metal (Kohan, 1997). One solution is to prevent oxygen from entering the system.

Feedwater, makeup water, and returned condensate can be physically deaerated— removal of air, including oxygen— to remove over 99% of non-condensable gases (Jackson, 1987), with some systems capable of removing oxygen to as low as 6.5 parts per billion (ppb) (Betz, 1980). The level is generally considered to result in negligible corrosion with little upkeep for most equipment (Matthews, 1951).

Some fuels are more likely to lead to oxygen corrosion than others. Replacement with a cleaner burning fuel can reduce corrosion (Payne, 1989). This more frequently reduces corrosion on the external wall that is heated (the fireside) than on the internal wall that contains the water that is heated to produce steam (the waterside). Air fed for fuel can be a source of free oxygen in the water of some systems. Low oxygen combustion— running a richer mix— can reduce oxygen found in the feedwater of these systems. However, this approach can also reduce fuel efficiency. Using a nitrogen blanket can reduce the amount of oxygen in a tube or tank that is shutdown for maintenance (Basu, Kefa, and Jestin, 2000). Naturally occurring tannins can also remove oxygen from boiler water (Matthews, 1951). Corrosion inhibitors are substances that added to the environment in which a metal corrodes. These are often metals that can be sacrificed to protect other metals (Moran and Natishan, 1993).

Oxygen Scavengers

Several substances are added to water to react with free oxygen (O_2) to remove it from suspension in water. These are known as '*oxygen scavengers*' and are generally highly reactive and volatile compounds (Kohan, 1997). The most commonly used scavenger for corrosion inhibition is sodium sulfite, usually combined with a catalyst (Schroeder, 1991). Others include ethylenediaminetetraacetic acid (EDTA) and nitriloacetic acid (NTA).

Ascorbic acid is also reportedly used as an oxygen scavenger by food processors (Bellows, 1997). Ascorbic acid used in combination with activated carbon scavenges oxygen from boiler condensate (May, 1989). Citric acid is also reportedly used. Like ascorbic acid, citric acid is not listed in 21 CFR 173.310, but is a direct food additive that is Generally Recognized As Safe (GRAS) with no limitations other than current good manufacturing practice (21 CFR 184.1033).

Corrosion is due to the following:

1. Corrosion of iron in water
2. Oxygen (dissolved oxygen in water)
3. Carbon dioxide corrosion

The rate of both boiler and condensate corrosion can be influenced by the following in-plant approaches:

1. Mechanical deaeration of the feed water is an important first step in eliminating dissolved gases such as oxygen and other corrosive gases such as ammonia, carbon dioxide and hydrogen sulfide.
2. Application of a non-volatile chemical deaerator such as sodium sulfite that is easy to handle, relatively non-toxic, and readily removed by precipitation or ion exchange. Oxygen removal takes place according to the following equation:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

(The sodium sulfate formed is non-scaling)

3. Removal of carbonate and bicarbonate components of the water by ion exchange prior to entering the boiler system.

Note that sodium sulfite has *not* been reviewed by the NOSB and that sulfites are prohibited by the Organic Foods Production Act (7 USC 6510(a)(3)). However, because it is non-volatile, there is relatively little carry over of sulfites, with excess remaining in the boiler or feedwater (Betz, 1980). Therefore, such an application would be thought of as a processing aid for a non-organic ingredient, and not in contact with the organic food itself.

Volatile Amines

Amines are derivatives of ammonia (NH_3) where a radical (R) that contains carbon replaces one or more of the hydrogen atoms ($R\text{-}NH_2$). Amines are classified as *primary, secondary*, or *tertiary* depending on the number of hydrogens replaced by radicals (Streitweiser and Heathcock, 1985). These radicals may be alkanols, such as diethylaminoethanol (DEAE), cyclic hydrocarbons (cyclohexylamine), fatty acids such as stearic acid (octadecylamine), or lower aliphatic (open chain) compounds (morpholine).

Volatile amines are characterized by their high solubility in water and reactivity. These very chemical properties that make them effective as boiler water additives make them extremely difficult to remove from the steam. Therefore it is practically impossible to prevent volatile amines from coming into contact with food if those additives are being used to treat the boiler water that generates the steam. Their ability to form 'azeotropes' or solutions that have the same boiling point as water, and therefore cannot be separated by distillation makes it difficult to remove them from the steam once introduced. The petroleum industry pioneered the use of volatile amines for corrosion control in the petroleum industry in the 1940s. These compounds were adopted for use in nuclear reactors during the 1950s and 1960s (Nathan, 1965).

Early references to the initial applications of volatile amines to food processing are scarce. The introduction of volatile amines to food handling presented a number of engineering challenges. Researchers found that periodic addition caused fluctuations between undetectable and high levels. Amines that were below the detection limit indicated that the equipment was not protected from corrosion. High levels were undesirable both because it was inefficient to use excessive amounts and the residues posed a threat to food safety. Researchers found that continuously metered addition of volatile amines could maintain the carry over to relatively low levels (Malaiyandi, Thomas, and Meek, 1979). While petroleum refineries and nuclear reactors could continuously stream amines with little concern for an upper limit, food processing and hospital applications required reliable and precise injection equipment able to maintain levels at or below what was considered minimal and acceptable to protect human health.

Systems that capture and recirculate the steam are called *condensate systems.* These systems can be more energy efficient and can also conserve water. They are also considered more complicated to operate and are higher maintenance. They are particularly susceptible to oxygen corrosion. Condensate systems can be chemically treated to reduce metal loss caused by oxygen and carbon dioxide corrosion. The treatment chemicals consist of neutralizing amines, filming amines and ammonia.

Neutralizing ($R\text{-}NH_2$) amines react with the acid (H^+) generated by the solution of carbon dioxide from the condensate according to the following equation (Betz, 1980):

$$R\text{-}NH_2 + H_2CO_3 \rightarrow R\text{-}NH_3 + HCO_3$$

Creating a condensate pH of 8.5 to 9.0

There are numerous amines that can be used for condensate pH neutralization and elevation. The selection of the appropriate amine is controlled by their stability and distribution ratio characteristics of the particular amine.

The distribution ratio of an amine is defined as:

$$DR = \frac{\text{amine in vapor phase}}{\text{amine in water phase (condensate)}}$$

Amines with a distribution ratio greater than 1.0 have more amine in the vapor phase than in the water phase.
The distribution ratios at atmospheric pressure of FDA approved neutralizing amines are:

Morpholine-	0.4
Diethylamino ethanol-	1.7
Cyclohexylamine-	4.0
Ammonia-	10.0

(Source: Betz, 1980).

The principle advantage of volatile amines over caustics is their ability to travel the length of the steam conduction equipment. This also means that they carry over into the food. Another approach to preventing steam condensate line corrosion is the use of amines whose primary function is to create a film or coating when formulated with emulsifiers and dispersants. Filming amines provide protection from both carbon dioxide and oxygen. The major FDA approved amine for this purpose is octadecylamine. Like the other volatile amines, octadecylamine will carry over into steam that comes into contact with food.

Organic processors that use culinary steam want to protect their equipment from premature corrosion and wear. A review of the different standards and interviews with different certifiers shows that organic processors and their certifiers have responded in different ways to the NOSB's recommended prohibition on boiler chemicals in contact with organic food (NOSB, 1995). Some certifiers have required steam treated with volatile amines be required to go through 'blow down' or the removal of concentrated boiler water and solid residues from a boiler system before it can commence to process organic food by using steam generated from fresh water without additives. Blow down is an important part of any boiler maintenance program (Kohan, 1997). However, frequent starts and stops can cause wear and tear on a boiler (Montrone and Blough, 1989).

Others require that the injection system for the treatment chemicals be shut off, where possible. To clear the system of prohibited substances the processor may need to run a flush of organic product not sold as 'organic.' The interruption of treatment can also cause damage to a system (Montrone and Blough, 1989). Some organic processors have installed filters or steam traps. These in-line filters may be a minimum of 10 microns to prevent residues from boiler chemicals from entering food necessary on culinary steam lines. While these may remove mechanical carryover, they will not remove vaporous carryover.

Corrosion prevention in organic processing systems rely primarily on the installation of corrosion-resistant equipment, mechanical and physical control of factors that contribute to corrosion, and the use of additives that do not have vaporous carry over or where vaporous carry over can be removed by entrained water. Physical deaeration in combination with chemical deaeration with sodium sulfite in addition to removal of alkalinity components such as carbonate and bicarbonate may offer a short-term alternative to the use of volatile amines, provided that steps are taken to prevent carry over of sulfites. More research should be done to develop long-term sustainable alternatives.

Conclusion

The TAP reviewed the neutralizing and filming amines petitioned. A review of the current state of the technology and existing organic standards supports the NOSB's recommendation for boiler water additives in Organic Good Manufacturing Practices. Residues of boiler water additives must be prevented from contacting organically produced food by the use of steam without entrained water, steam filtering, or other means. Volatile amines are made to carry over in the steam and are not practical to remove by the methods described. The TAP reviewers advised that none of the boiler water additives in that category be added to the National List. Therefore, the NOSB may want to consider amending the recommendation for Organic Good Manufacturing Practices to categorically prohibit volatile amines used as boiler water additives.

Appendix I

Existing Standards for Boiler Water Additives in Organic Food Processing

National Organic Standards Board (NOSB)
g) Boiler Water Additives (refer to 21 CFR Part 173.310(a))
"Residues of boiler water additives must be prevented from contacting organically produced food by the use of steam without entrained water, steam filtering, or other means" (NOSB, 1995).

Organic Crop Improvement Association (OCIA)
5.2.4. CULINARY STEAM USAGE GUIDELINES
If culinary steam is used during any part of food processing, then steam condensate traps shall be placed to collect condensate for testing of known used boiler chemicals. At least one trap should be placed as close to the first entry of steam into the food system as possible.
a. Steam filters should be required for food contact steam.
b. Testing for the presence of prohibited substances used in boiler water conditioning shall be mandatory if culinary steam is used during any part of an organic food process and comes in contact with the food and no filters are employed to remove said substances prior to the steam contacting the food.
c. Steam condensate testing shall be for the specific material used in that particular boiler system and should be conducted by any state of federally accredited testing facility.
d. Limits on tested substances shall be non-detectable to the limit of the equipment used.
Recommendations:
1. All boiler systems should be on a monthly service schedule by a professional water conditioning company which tests treatment limits and operating conditions peculiar to that boiler.
2. Typical boiler operating parameters should be no more than 80% of capacity.
3. Condensate traps need to be installed at appropriate junctions to provide sampling of steam quality and purity. (OCIA, 2000).

From the OCIA list:
Steam A Steam in contact with food may not contain boiler chemicals and subject to the requirement of OCIA Standard 5.2.4. (OCIA, 2000).

Oregon Tilth Certified Organic (OTCO)
Volatile boiler chemicals--including amines such as cyclohexylamine, diethyleaminoethanol, hydrazine, and morpholine--were prohibited effective January 1, 2000 (Coody, 1998). This is consistent with their April 1999 Generic Materials List (OTCO, 1999).

Quality Assurance International (QAI)
(A120-99321) on the QAI website:
"7.14. Boiler Additives. Steam from boiler water, which contains additives, is not allowed to come into contact with any organic product." (QAI, 2000).

European Union
Organic processing must be done in such a manner as to prevent contamination or accidental substitution of organic and non-organic food products. The only processing aids permitted must appear on a closed list. Preference is given to plants and equipment dedicated to organic processing. In a non-dedicated plant, equipment is usually required to be dismantled and cleaned before an organic run when possible. Where this is not possible, the equipment is subject to a 'bleed run' (product flush) of the organic product to purge the system of residues (Michaud, Redman, and Dalby, 1994).

Appendix II
Boiler Water Additives and their Current Organic Status

Substances	CAS #	FDA Limitations[1] / *NOP Annotations*[2]	National List[2]
Acrylamide-sodium acrylate resin	---	Contains not more than 0.05 percent by weight of acrylamide monomer.	No
Acrylic acid/2-acrylamido-2-methyl propane sulfonic acid copolymer having a minimum weight average molecular weight of 9,900 and a minimum number average molecular weight of 5,700.	---	Total not to exceed 20 parts per million (active) in boiler feedwater.	No
Ammonium alginate	9005-34-9	----	Yes
Cobalt sulfate	10124-43-3	As catalyst	No
1-hydroxyethylidene-1,1-diphosphonic acid and its sodium and potassium salts.	2809-21-4	(CAS Reg. No.)	No
Lignosulfonic acid	8062-15-5	*As [a] floating agent in postharvest handling*	Annotated
Monobutyl ethers of polyethylene- polypropylene glycol produced by random condensation of a 1:1 mixture by weight of ethylene oxide and propylene oxide with butanol.	---	Minimum mol. wt. 1,500.	No
Poly(acrylic acid-co-hypophosphite), sodium salt produced from a 4:1 to a 16:1 mixture by weight of acrylic acid and sodium acid monomer (dry weight basis).	71050-62-9	Total not to exceed 1.5 parts per million in boiler feed water. Copolymer contains not more than 0.5 percent by weight of acrylic hypophosphite.	No
Polyethylene glycol	25322-68-3	As defined in 21 CFR 172.820	No
Polymaleic acid	26099-09-2	Total not to exceed 1 part per million in boiler feed water (calculated as the acid).	No
Polymaleic acid and its Sodium salt	30915-61-8	Total not to exceed 1 part per million in boiler feed water (calculated as the acid).	No
Sodium salt of polymaleic acid	70247-90-4	Total not to exceed 1 part per million in boiler feed water (calculated as the acid).	No
Polyoxypropylene glycol	---	Minimum mol. wt. 1,000.	No
Potassium carbonate	584-08-7	---	Yes
Potassium tripolyphosphate	13845-36-8	---	No
Sodium acetate	127-09-3	---	No
Sodium alginate	9005-38-3	---	Yes
Sodium aluminate	1302-42-7	---	No
Sodium carbonate	497-19-8	---	Yes

Substances	**CAS #**	**FDA Limitations[1] /** *NOP Annotations[2]*	**National List[2]**
Sodium carboxymethylcellulose	9004-32-4	Contains not less than 95 percent sodium carboxymethylcellulose on a dry-weight basis, with maximum substitution of 0.9 carboxymethylcellulose groups per anhydroglucose unit, and with a minimum viscosity of 15 centipoises for 2 percent by weight aqueous solution at 25 deg.C.	No
Sodium glucoheptonate	---	Less than 1 part per million cyanide in the sodium glucoheptonate.	No
Sodium hexametaphosphate	10124-56-8	*For use only in dairy foods.*	Annotated
Sodium humate	---	---	No
Sodium hydroxide	7775-14-6	*Prohibited for use in lye peeling of fruits and vegetables.*	Annotated
Sodium lignosulfonate	8061-51-6	*As [a] floating agent in postharvest handling*	Annotated
Sodium metabisulfite	7681-57-4	---	No
Sodium metasilicate	6834-92-0	*See 7 CFR 205.601(l).*	No
Sodium nitrate	7632-00-0	---	No
Monosodium phosphate	7558-80-7	*For use only in dairy foods.*	Annotated
Trisodium phosphate	7601-54-9	*For use only in dairy foods.*	Annotated
Disodium phosphate	7558-79-4	*For use only in dairy foods.*	Annotated
Sodium polyacrylate	---	---	No
Sodium polymethacrylate	54193-36-1		No
Sodium silicate	1344-09-8	*As [a] floating agent in postharvest handling*	No
Sodium sulfate	7757-82-6	---	No
Sodium sulfite	7757-83-7	Neutral or alkaline.	No
Sodium tripolyphosphate	7758-29-4	*For use only in dairy foods.*	Annotated
Tannin	1401-55-4	Including quebracho extract.	No
Tetrasodium EDTA	64-02-8	---	No
Tetrasodium pyrophosphate	7722-88-2	*For use only in dairy foods.*	Annotated
Cyclohexylamine	108-91-8	Not to exceed 10 parts per million in steam, and excluding use of such steam in contact with milk and milk products.	No
Diethylaminoethanol	100-37-8	Not to exceed 15 parts per million in steam, and excluding use of such steam in contact with milk and milk products.	No
Hydrazine	302-01-2	Zero in steam.	No
Morpholine	110-91-8	Not to exceed 10 parts per million in steam, and excluding use of such steam in contact with milk and milk products.	No
Octadecylamine	124-30-1	Not to exceed 3 parts per million in steam, and excluding use of such steam in contact with milk and milk products.	No
Trisodium nitrilotriacetate	5064-31-3	Not to exceed 5 parts per million in boiler feedwater; not to be used where steam will be in contact with milk and milk products.	No

Sources: [1]21 CFR 173.310; [2]7 CFR 205.601(l) and 7 CFR 205.605.

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Corrosion Consequences of Water Treatment Upsets

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*wo case histories of carbon-steel boiler tube failures are
esented in this article. One covers gouging of an evapo-
tor tube in an atmospheric, fluidized bed combustion
it operating with free caustic in the water. The other
ustrates underdeposit corrosion and hydrogen damage
w all tubing in a conventional utility boiler. Wa-
qu..ty control and adequate component monitoring
ll help to combat these failures.*

V arious industry surveys have indicated that a major cause of steam generator downtime is
failure of tubular components.[1] Materials degra-
ion by the operating environment as a result of
-side or water/steam-side corrosion is the pri-
ry factor responsible for these failures. In the
e of water/steam-side corrosion, ever-improving
ler and feedwater treatment systems have been
oduced to lessen this type of attack. However,
e failures continue to result from inadequate
mical control and operating conditions, which
et water quality and diminish the effectiveness
uch treatment.

Case Histories

The following examples illustrate the types of
res investigated and their associated mecha-
ıs.

1: Atmospheric Fluidized Bed Combustion (AFBC) Evaporator Tube

\ft. pproximately 600 hours of operation in
FBC unit, an evaporator tube ruptured during
ce. The carbon-steel tube, which was designed
-bed operation at 12.2 MPa (1770 psig), had externally welded longitudinal fins at the 4-, 6-, 8-, and 12-o'clock locations, as well as ball studs between the three underside fins. A pinhole failure had occurred adjacent to the upper fin weld, but there was no external wear apparent in the vicinity of the hole.

A portion of the failed tube was sectioned for further examination. A longitudinal depression approximately 25 mm (1 in.) wide was evident on the inside surface beneath the upper fin (Figure 1). A transverse cross section taken a short distance from the perforation illustrated the groove-like wall thinning that had occurred in the area (Figure 2).

The groove contained a hard, tenacious, dark deposit, confirmed as magnetite (Fe_3O_4) by x-ray diffraction. Microscopic inspection of the deposit revealed it was relatively porous (Figure 3).

Further examination of the deposit at various locations using a scanning electron microscope (SEM) equipped with an energy-dispersive x-ray analyzer (EDAX) disclosed:

- The bulk deposit was predominantly iron, with a small amount of manganese
- A tan deposit that attended the groove was high in calcium and sulfur with a small concentration of iron and a trace of phosphorous
- Copper-rich islands were noted in the polished cross sections.

The EDAX determined that solids from the boiler water had deposited on the tube surface and were comingled with the corrosion product (magnetite). The particles may have originated as a preboiler corrosion product, minerals in the water,

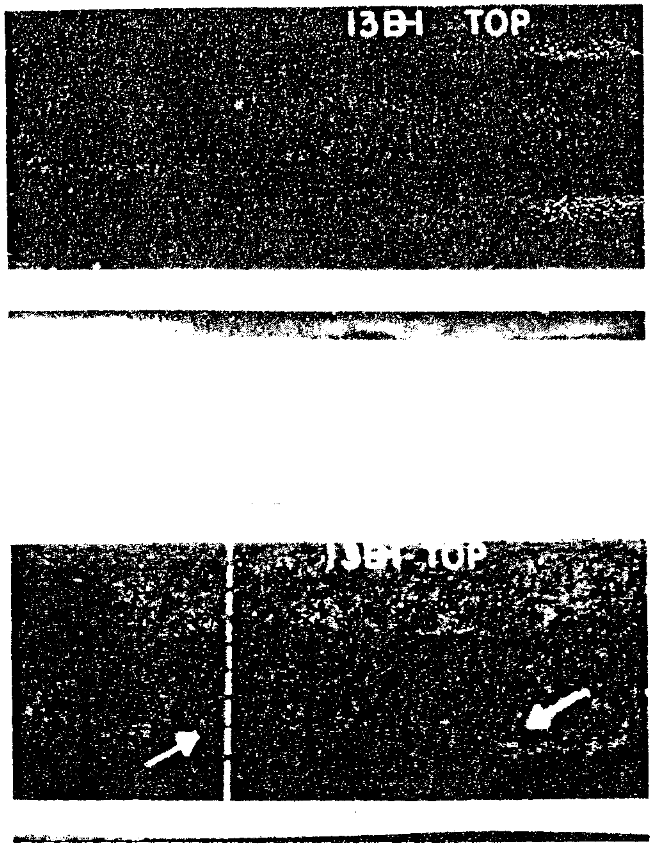

FIGURE 1
Inside surface of top half of tube. Note groove and perforations in wall at two locations in groove, indicated by arrows; a transverse cross section (Figure 2) was removed through location indicated by dashed line.

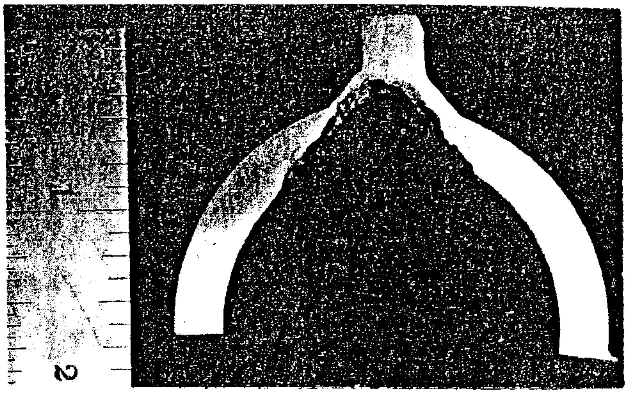

FIGURE 2
Transverse cross section cut through location shown in Figure 1.

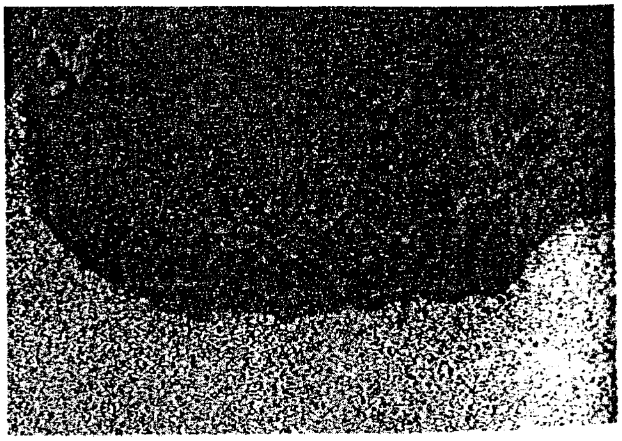

FIGURE 3
Microscopic appearance of porous, dark, tenacious deposit in groove.

boiler water treatment chemicals, or combinations of these.

Since the unit uses a caustic-phosphate boiler water treatment, and since the grooves displayed the manifestations of caustic attack, the primary mechanism of metal wastage was attributed to caustic corrosion. For this mechanism to operate, caustic (NaOH) must be concentrated at the tube surface. The resultant high pH causes a breakdown of the protective iron-oxide layer on the tube surface, allowing corrosion to proceed rapidly.

Caustic can be concentrated under porous deposits that develop on internal tube surfaces. The deposits form when dissolved or suspended solids in the water drop out and foul the tube surfaces, particularly in areas subjected to a high heat flux. The corrosiveness of the deposits depends on the quality and control of the boiler water treatment process. If no free caustic is present, the deposits are innocuous.

If free caustic is present, however, the following can occur. As boiler water continuously seeps through the deposit and is boiled off at the tube surface, the deposit becomes concentrated with caustic. Since the caustic in the deposit is more concentrated, the next volume of water that seeps through also becomes concentrated with caustic. The process repeats itself until the water develops the locally high caustic concentrations that cause metal wastage. The resultant corrosion product further aggravates the condition by thickening the layer of scale/deposit already on the tube surface. This thicker layer not only provides more surface area for deposit concentration, but also raises the tube-wall temperature, thereby accelerating the concentrating mechanism. The fin at the top of the tube results in a higher heat flux and increases the local tube-wall temperature, producing an even greater concentrating effect under the fin.

A review of the plant history disclosed frequent start-ups and shutdowns during operation.[2] Thus, water treatment practice was unstable, and free

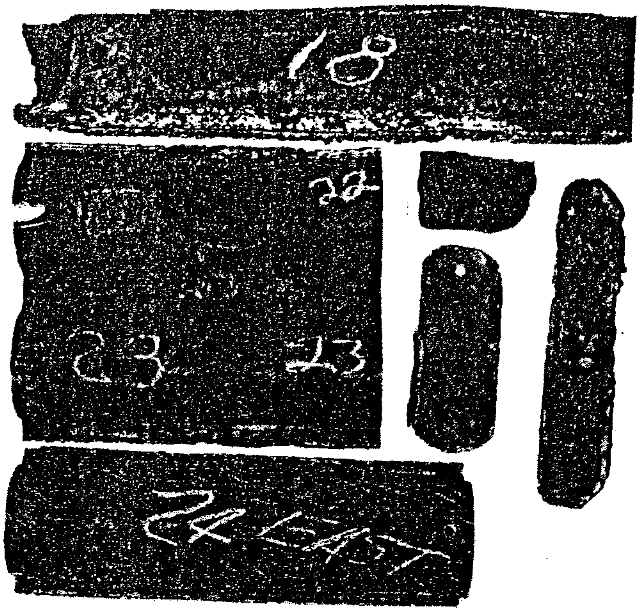

FIGURE 4
Sections of tubes 18, 22, 23, and 24 and segments flame cut from tubes 22 and 23. Note window opening in tube 22.

caustic was present in the boiler most of the time. No caustic gouging was evident in an adjacent cell of the unit, which had not been operated when the water chemistry was upset.

As a result of the failure, improved control of feedwater was implemented and turbulators were installed in the vaporator tubing to avoid steam blanketing under the top fin.

Case 2: Utility Boiler Waterwall Tubes

Hydrogen damage can result in an intergranular brittle-type fracture of carbon-steel tubing. The fracture surfaces are typically thick-edged, and many times a "window opening," outlining the area of hydrogen-damaged steel, is blown out. The hydrogen damage begins with the formation of an internal deposit, but the deposit may subsequently be washed from the surface by turbulent water and escaping steam during the failure.

The internal fouling of a heat-transfer surface provides a collection site for boiler water chemicals and, because of the insulating effect, causes a localized higher metal temperature. If an acidic solution develops under the deposit, the resultant corrosion liberates atomic hydrogen. The atomic hydrogen migrates through the tube wall, where it can collect at imperfections or combine with iron carbide (Fe_3C) at the grain boundaries to form methane according to the formula:

$$Fe_3 + 4H \leftrightarrow CH_4 + 3Fe \qquad (1)$$

The methane formation can cause decarburization and, as the methane pressure builds, discontinuous microfissures can also form. As the mechanism progresses, the fissures link up to cause a through-wall fracture in a brittle manner.^{3}

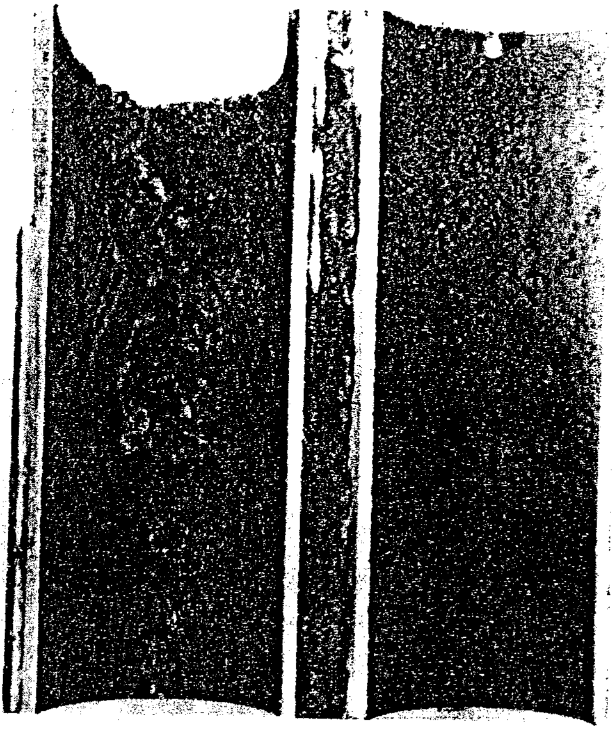

FIGURE 5
Corrosion and deposit on inside surfaces of tube 18 (fire-side face [left] and back of tube [right]).

Both hydrogen damage and caustic attack result from corrosion and the accompanying evolution of hydrogen, but the location of hydrogen evolution, as well as pH condition, is different. The hydrogen evolution with caustic gouging is at the edge of the deposit, where it can be easily dispersed in the flowing medium. In the case of hydrogen damage, the solution under the deposit is acidic, and hydrogen evolves under the deposit close to the anodic and cathodic sites. This evolution results in more concentrated hydrogen and its resultant greater migration into the steel.

A recent failure of carbon-steel waterwall tubing after seven years of operation in a utility boiler further emphasizes the relationship between acidic conditions and hydrogen damage. Sections of four tubes from this boiler (numerically identified as tubes 18, 22, 23, and 24) were examined. A discussion of this investigation follows.

The submitted sections of the waterwall tubes are shown in Figure 4. Several areas of tubes 18, 22, and 23 exhibited corroded regions on the inside surfaces (note window-type failure in tube 22). Tube 24 had not suffered the attack. The appearance of a corroded zone on the inside surface of tube 18 is illustrated in Figure 5. The deposits that covered

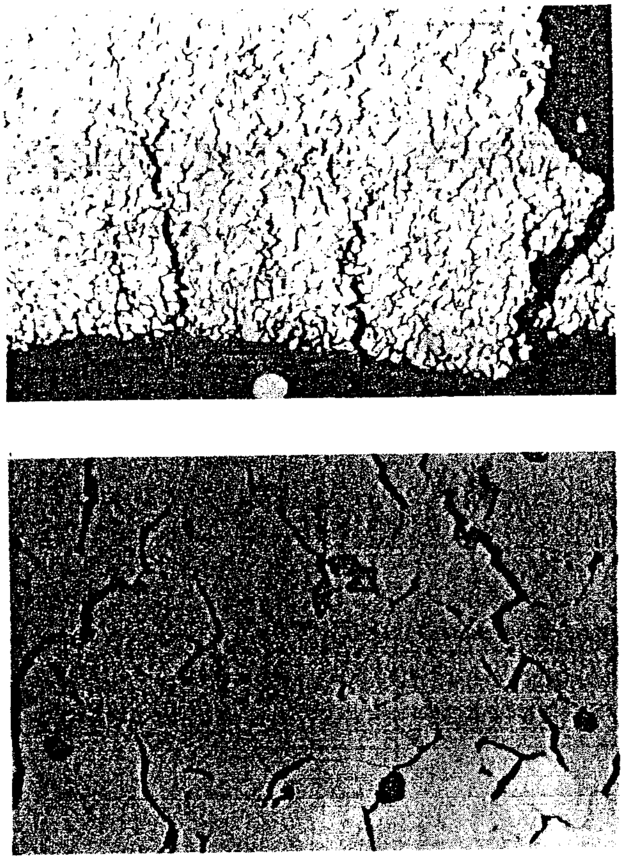

FIGURE 6
Inside surface of tube 23 at corroded region, showing extensive hydrogen damage.

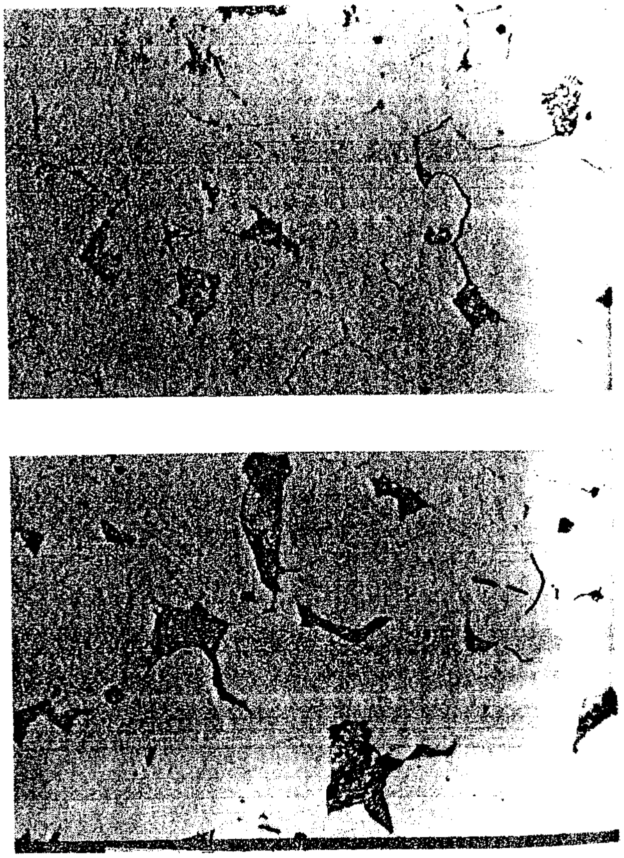

FIGURE 7
Microstructure in fire-side face (top) at corroded inside surface and in wall diametrically opposite in tube 18 (bottom). Carbides in pearlite grains in fire-side face had started to spheroidize.

the corroded zones were approximately 3 mm (1/8 in.) thick.

Representative cross sections were taken through corroded inside surface areas and uncorroded zones of tubes 18, 22, and 23. Extensive hydrogen damage, illustrated in Figure 6, was detected at one corroded region of tube 23. The microstructures at diametrically opposed outside surfaces of tube 18 (Figure 7) indicate slight overheating to a metal temperature of approximately 454 to 482°C (850 to 900°F) on the fire side.

Deposit samples from the inside surfaces of tubes 23 and 18 in the corroded zones were analyzed by EDAX. Chlorides (probably an iron-chloride corrosion product) were present on the surface of tube 23, where hydrogen damage was found. The regions that suffered corrosion, but where no chlorides were present, were free of hydrogen damage. The outer layer (farthest from inside tube surface) contained sizable quantities of copper, as well as calcium, phosphorous, magnesium, zinc, nickel, and sulfur. The middle of the deposit was composed predominantly of iron oxide.

An examination of the submitted tube sections disclosed that portions of the inside surfaces of tubes 18, 22, and 23 had been exposed to corrosive attack. The attack was on the fire-side faces of the tubes. A moderately thick deposit/corrosion product was present on the corroded surfaces. In one region of tube 23, both hydrogen damage and corrosion had caused the failure.

Analysis of the deposit/corrosion product in the area that suffered hydrogen damage and another corroded area that was free of hydrogen damage disclosed the presence of chlorine solely at the hydrogen damaged area. The presence of a chloride (apparently iron chloride, a corrosion product) had developed an acidic condition at the corroded surface that caused the hydrogen damage.

Possibly the corrosion of the inside surfaces of the tubes was initiated by the deposition of calcium, iron, and magnesium phosphate, as well as copper, nickel, and zinc. Boiler water seeped through the deposit to the tube surface, which was now at a slightly elevated temperature. In one instance the metal temperature was estimated to have been approximately 482°C (900°F). This overheat was indicated by the minor change in microstructure detected in the fire-side face of tube 18. The boiler water treatment chemicals became concentrated at the overheated wall, causing corrosion of the tube wall and development of a corrosion product. If chlorides or other acid-forming constituents had been present, hydrogen damage could result; in the absence of an acid-forming constituent, only corrosion of the tube wall occurred.

Correction of the water upset, condenser leakage, or a combination, as well as removal of the deposits by acid cleaning, was recommended to avoid future deposit formation.

Conclusions

Corrosion has been identified as a primary cause of tube failures in utility boilers. The mechanisms related to deposit formation, caustic attack, and hydrogen damage described in this article can occur—even when adequate water treatment programs are specified. To minimize the costly damage associated with such failures, care must be exercised to ensure proper water quality control and adequate component monitoring in light of operating excursions and system upsets.

Acknowledgments

The authors express gratitude to J. Cocubinsky, G. Stanko, and I. Dojcsanszky for their efforts in conducting the failure analyses that are the basis for this article.

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More information may be obtained from CORROSION/89 paper no. 72, presented in New Orleans, Louisiana.

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NACE standards provide information on recommended procedures, design methods, installation, maintenance, laboratory methods and selection of materials and corrosion control systems. Sixty-six standards have been developed to date.

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- RP0178-89 — Design, Fabrication, Surface Finish Requirements and Proper Design Considerations for Tanks and Vessels to be Lined for Immersion Service (Sponsored by NACE Task Group T-6G-27)
- RP0189-89 — On-line Monitoring of Cooling Waters (Sponsored by NACE Task Group T-3T-1)

Look for the following standards to be published in 1990:

- Test Method, "Impressed Current Test Method for Laboratory Testing of Aluminum Anodes" (Sponsored by NACE Task Group T-7L-2)
- Recommended Practice, "Cathodic Protection of Reinforcing Steel in Atmospherically Exposed Concrete Structures" (Sponsored by NACE Task Group T-3K-2)
- Recommended Practice, "Maintenance and Rehabilitation Considerations for Corrosion Control of Existing Steel Reinforced Concrete Structures" (Sponsored by NACE Task Group T-3K-5)
- "Recommended Practices on Deaerator Cracking" (Sponsored by NACE Task Group T-7H-7)
- Revision to NACE Standard TM0374-74, "Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution" (Sponsored by NACE Task Group T-1D-31)
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(b) The component substances are used solely as a solvent mixture and in a manner that does not result in formation of products not present in conventionally produced citric acid.

(c) The citric acid so produced meets the specifications of the "Food Chemicals Codex," 3d Ed. (1981), pp. 86-87, which is incorporated by reference (copies may be obtained from the National Academy Press, 2101 Constitution Ave. NW., Washington, DC 20418, or may be examined at the Office of the Federal Register, 800 North Capitol Street, NW., suite 700, Washington, DC 20408), and the polynuclear aromatic hydrocarbon specifications of § 173.165.

(d) Residues of *n*-octyl alcohol and synthetic isoparaffinic petroleum hydrocarbons are removed in accordance with good manufacturing practice. Current good manufacturing practice results in residues not exceeding 16 parts per million (ppm) *n*-octyl alcohol and 0.47 ppm synthetic isoparaffinic petroleum hydrocarbons in citric acid.

(e) Tridodecyl amine may be present as a residue in citric acid at a level not to exceed 100 parts per billion.

[42 FR 14491, Mar. 15, 1977, as amended at 49 FR 10106, Mar. 19, 1984]

§ 173.290 Trichloroethylene.

Tolerances are established for residues of trichloroethylene resulting from its use as a solvent in the manufacture of foods as follows:

Decaffeinated ground coffee.	25 parts per million.
Decaffeinated soluble (instant) coffee extract.	10 parts per million.
Spice oleoresins	30 parts per million (provided that if residues of other chlorinated solvents are also present, the total of all residues of such solvents in spice oleoresins shall not exceed 30 parts per million).

Subpart D—Specific Usage Additives

§ 173.300 Chlorine dioxide.

Chlorine dioxide (CAS Reg. No. 10049-04-4) may be safely used in food in accordance with the following prescribed conditions:

(a) The additive is generated by treating an aqueous solution of sodium chlorite with either chlorine gas or a mixture of sodium hypochlorite and hydrochloric acid. The generator effluent contains at least 90 percent (by weight) of chlorine dioxide with respect to all chlorine species as determined by Method 4500-ClO_2 E in the "Standard Methods for the Examination of Water and Wastewater," 18th ed., 1992, or an equivalent method. Method 4500-ClO_2 E is incorporated by reference in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies are available from the Center for Food Safety and Applied Nutrition (HFS-200), Food And Drug Administration, 200 C St., SW., Washington, DC 20204-0001 and The American Public Health Association, 1015 Fifteenth St., NW., Washington, DC 20005, or may be examined at the Office of the Federal Register, 800 North Capitol St., NW., suite 700, Washington, DC.

(b)(1) The additive may be used as an antimicrobial agent in water used in poultry processing in an amount not to exceed 3 parts per million (ppm) residual chlorine dioxide as determined by Method 4500-ClO_2 E, referenced in paragraph (a) of this section, or an equivalent method.

(2) The additive may be used as an antimicrobial agent in water used to wash fruits and vegetables that are not raw agricultural commodities in an amount not to exceed 3 ppm residual chlorine dioxide as determined by Method 4500-ClO_2 E, referenced in paragraph (a) of this section, or an equivalent method. Treatment of the fruits and vegetables with chlorine dioxide shall be followed by a potable water rinse or by blanching, cooking, or canning.

[60 FR 11900, Mar. 3, 1995. Redesignated at 61 FR 14245, Apr. 1, 1996, as amended at 61 FR 14480, Apr. 2, 1996; 63 FR 38747, July 20, 1998]

§ 173.310 Boiler water additives.

Boiler water additives may be safely used in the preparation of steam that will contact food, under the following conditions:

(a) The amount of additive is not in excess of that required for its functional purpose, and the amount of steam in contact with food does not exceed that required to produce the intended effect in or on the food.

(b) The compounds are prepared from substances identified in paragraphs (c) and (d) of this section, and are subject to the limitations, if any, prescribed:

(c) List of substances:

Substances	Limitations
Acrylamide-sodium acrylate resin	Contains not more than 0.05 percent by weight of acrylamide monomer.
Acrylic acid/2-acrylamido-2-methyl propane sulfonic acid copolymer having a minimum weight average molecular weight of 9,900 and a minimum number average molecular weight of 5,700 as determined by a method entitled "Determination of Weight Average and Number Average Molecular Weight of 60/40 AA/AMPS" (October 23, 1987), which is incorporated by reference in accordance with 5 U.S.C. 552(a). Copies may be obtained from the Center for Food Safety and Applied Nutrition (HFS–200), Food and Drug Administration, 200 C St. SW., Washington, DC 20204, or may be examined at the Office of the Federal Register, 800 North Capitol Street, NW., suite 700, Washington, DC.	Total not to exceed 20 parts per million (active) in boiler feedwater.
Ammonium alginate.	
Cobalt sulfate (as catalyst).	
1-hydroxyethylidene-1,1-diphosphonic acid (CAS Reg. No. 2809–21–4) and its sodium and potassium salts.	
Lignosulfonic acid.	
Monobutyl ethers of polyethylene-polypropylene glycol produced by random condensation of a 1:1 mixture by weight of ethylene oxide and propylene oxide with butanol.	Minimum mol. wt. 1,500.
Poly(acrylic acid-*co*-hypophosphite), sodium salt (CAS Reg. No. 71050–62–9), produced from a 4:1 to a 16:1 mixture by weight of acrylic acid and sodium hypophosphite.	Total not to exceed 1.5 parts per million in boiler feed water. Copolymer contains not more than 0.5 percent by weight of acrylic acid monomer (dry weight basis).
Polyethylene glycol	As defined in § 172.820 of this chapter.
Polymaleic acid [CAS Reg. No. 26099–09–2], and/or its sodium salt. [CAS Reg. No. 30915–61–8 or CAS Reg. No. 70247–90–4].	Total not to exceed 1 part per million in boiler feed water (calculated as the acid).
Polyoxypropylene glycol	Minimum mol. wt. 1,000.
Potassium carbonate.	
Potassium tripolyphosphate.	
Sodium acetate.	
Sodium alginate.	
Sodium aluminate.	
Sodium carbonate.	
Sodium carboxymethylcellulose	Contains not less than 95 percent sodium carboxymethylcellulose on a dry-weight basis, with maximum substitution of 0.9 carboxymethylcellulose groups per anhydroglucose unit, and with a minimum viscosity of 15 centipoises for 2 percent by weight aqueous solution at 25 °C; by the method prescribed in the "Food Chemicals Codex," 4th ed. (1996), pp. 744–745, which is incorporated by reference in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies are available from the National Academy Press, Box 285, 2101 Constitution Ave. NW., Washington, DC 20055 (Internet address "http://www.nap.edu"), or may be examined at the Center for Food Safety and Applied Nutrition's Library, Food and Drug Administration, 200 C St. SW., rm. 3321, Washington, DC, or at the Office of the Federal Register, 800 North Capitol St. NW., suite 700, Washington, DC.
Sodium glucoheptonate	Less than 1 part per million cyanide in the sodium glucoheptonate.
Sodium hexametaphosphate.	
Sodium humate.	
Sodium hydroxide.	
Sodium lignosulfonate.	
Sodium metabisulfite.	
Sodium metasilicate.	
Sodium nitrate.	
Sodium phosphate (mono-, di-, tri-).	
Sodium polyacrylate.	
Sodium polymethacrylate.	
Sodium silicate.	
Sodium sulfate.	
Sodium sulfite (neutral or alkaline).	

Substances	Limitations
Sodium tripolyphosphate.	
Sorbitol anhydride esters: a mixture consisting of sorbitan monostearate as defined in § 172.842 of this chapter; polysorbate 60 ((polyoxyethylene (20) sorbitan monostearate)) as defined in § 172.836 of this chapter; and polysorbate 20 ((polyoxyethylene (20) sorbitan monolaurate)), meeting the specifications of the Food Chemicals Codex, 4th ed. (1996), pp. 306–307, which is incorporated by reference in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies are available from the National Academy Press, 2101 Constitution Ave. NW., Box 285, Washington, DC 20055 (Internet http://www.nap.edu), or may be examined at the Center for Food Safety and Applied Nutrition's Library, Food and Drug Administration, 200 C St. SW., rm. 3321, Washington, DC, or at the Office of the Federal Register, 800 North Capitol St. NW., suite 700, Washington, DC.	The mixture is used as an anticorrosive agent in steam boiler distribution systems, with each component not to exceed 15 parts per million in the steam.
Tannin (including quebracho extract).	
Tetrasodium EDTA.	
Tetrasodium pyrophosphate.	

(d) Substances used alone or in combination with substances in paragraph (c) of this section:

Substances	Limitations
Cyclohexylamine	Not to exceed 10 parts per million in steam, and excluding use of such steam in contact with milk and milk products.
Diethylaminoethanol	Not to exceed 15 parts per million in steam, and excluding use of such steam in contact with milk and milk products.
Hydrazine	Zero in steam.
Morpholine	Not to exceed 10 parts per million in steam, and excluding use of such steam in contact with milk and milk products.
Octadecylamine	Not to exceed 3 parts per million in steam, and excluding use of such steam in contact with milk and milk products.
Trisodium nitrilotriacetate	Not to exceed 5 parts per million in boiler feedwater; not to be used where steam will be in contact with milk and milk products.

(e) To assure safe use of the additive, in addition to the other information required by the Act, the label or labeling shall bear:

(1) The common or chemical name or names of the additive or additives.

(2) Adequate directions for use to assure compliance with all the provisions of this section.

[42 FR 14526, Mar. 15, 1977, as amended at 45 FR 73922, Nov. 7, 1980; 45 FR 85726, Dec. 30, 1980; 48 FR 7439, Feb. 22, 1983; 49 FR 5748, Feb. 15, 1984; 49 FR 10106, Mar. 19, 1984; 50 FR 49536, Dec. 3, 1985; 53 FR 15199, Apr. 28, 1988; 54 FR 31012, July 26, 1989; 55 FR 12172, Apr. 2, 1990; 61 FR 14245, Apr. 1, 1996; 64 FR 1759, Jan. 12, 1999; 64 FR 29227, June 1, 1999]

§ 173.315 Chemicals used in washing or to assist in the peeling of fruits and vegetables.

Chemicals may be safely used to wash or to assist in the peeling of fruits and vegetables in accordance with the following conditions:

(a) The chemicals consist of one or more of the following:

(1) Substances generally recognized as safe in food or covered by prior sanctions for use in washing fruits and vegetables.

(2) Substances identified in this subparagraph and subject to such limitations as are provided:

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PATENT FULL TEXT AND IMAGE DATABASE

United States Patent **5,830,383**
Greaves , et al. **November 3, 1998**

Method for inhibition of oxygen corrosion in aqueous systems by the use of a tannin activated oxygen scavenger

Abstract

A method of treating an aqueous system is described which comprises incorporating in the system a hydroxylamine derivative of the general formula: ##STR1## wherein each of R.sub.1, R.sub.2 and R.sub.3 which may be the same or different represents hydrogen, alkyl of 1 to 8 carbon atoms or aryl or a water soluble salt thereof or a precursor thereof, and a tannin in a weight ratio of at least 2:1. This is particularly useful for ***boiler*** water systems.

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Appl. No.:	**425689**
Filed:	**April 19, 1995**

Foreign Application Priority Data

Aug 17, 1992[GB]	9217448

Current U.S. Class:	**252/188.28**; 252/389.54; 252/392; 252/393; 252/395; 422/12; 422/13; 422/16; 422/19
Intern'l Class:	C02F 001/00; C09K 015/00
Field of Search:	252/188.28,392,393,395,389.54 422/13,12,16,19

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Parent Case Text

This is a continuation of application Ser. No. 08/107,550, filed Aug. 17, 1993, now abandoned.

Claims

We claim:

1. A composition suitable for addition to an aqueous system which comprises (i) at least one member of the group consisting of (a) a hydroxylamine or its derivatives, (b) water soluble salts and (c) precursors thereof having the formula: ##STR7## wherein each of R.sub.1, R.sub.2 and R.sub.3 may be the same or different is a member of the group consisting of hydrogen, alkyl of 1 to 8 carbon atoms, and aryl and (ii) a polyphenolic tannin selected from the group consisting of condensed tannin extracts from natural tannins, synthetic tannins and synthetic tannin derivatives wherein said tannin is present in an amount sufficient to have a catalytic effect on said hydroxylamine and (i) and (ii) are in a weight ratio of at least 2:1.

2. The composition according to claim 1 in which the hydroxylamine derivative is selected from the group consisting of an oxime and a nitrone.

3. The composition according to claim 1 in which the hydroxylamine is selected from a N-hydrocarbylhydroxylamine, a N,N-dihydrocarbylhydroxylamine or mixtures thereof.

4. The composition according to claim 1 in which the weight ratio of hydroxylamine derivative to tannin is from 3:1 to 20:1.

5. The composition according to claim 1 which comprises 5 to 50% by weight of hydroxylamine derivative as an aqueous solution.

6. The composition according to claim 1 in which said tannin is derived from mimosa, chestnut or quebracho.

7. The composition according to claim 1 which further contains a neutralized amine.

8. A composition suitable for addition to an aqueous system which consists essentially of (i) at least one member of the group consisting of (a) a hydroxylamine or its derivatives, (b) water soluble salts and (c)

precursors thereof having the formula: ##STR8## wherein each of R.sub.1, R.sub.2 and R.sub.3 may be the same or different is a member of the group consisting of hydrogen, alkyl of 1 to 8 carbon atoms, and aryl, and (ii) a polyphenolic tannin selected from the group consisting of condensed tannin extracts from natural tannins, synthetic tannins and synthetic tannin derivatives wherein said tannin is present in an amount sufficient to have a catalytic effect on said hydroxylamine and (i) and (ii) are in a ratio of at least 2:1 and a molybdate.

Description

This invention relates to a method of retarding or controlling corrosion in aqueous systems, especially ***boiler*** water systems, due to dissolved oxygen.

Dissolved oxygen is objectionable in water used for industrial purposes because of the corrosive effect on ferrous and yellow metals with which the water comes into contact. In cold and hot water lines, failure may occur in the piping and the lines may become blocked with the products of corrosion. "Red water" and iron stains may result caused by iron brought into solution by the corrosive attack of dissolved oxygen. It is well known that increased temperatures and low pH values accelerate oxygen attack.

In ***boiler*** systems dissolved oxygen is a principal factor influencing corrosion of metals which make up feed lines, heaters, economisers, boilers, and steam and return lines.

It is known to utilise oxygen scavengers for the purpose of eliminating the dissolved oxygen. These include sodium sulphite, hydrazine as well as hydroxylamine and derivatives. It will be appreciated that there are advantages in using a volatile oxygen scavenger i.e. one which does not result in any solid residues.

While sodium sulphite has been used for many years in low pressure boilers it cannot be used satisfactorily in high pressure boilers because it tends to decompose giving rise to acidic gases, principally sulphur dioxide and hydrogen sulphide which can give rise to corrosion. While hydrazine overcomes this difficulty it is a toxic chemical so that special precautions have to be taken over its use. More recently, therefore, use has been made of certain hydroxylamine derivatives, in particular N,N-diethylhydroxylamine. However, the use of such derivatives is not entirely satisfactory under all conditions because at relatively low temperatures its reaction with dissolved oxygen is rather slow. This becomes a particular problem when the derivative is added, as is normal, to the feed line in order to prevent corrosion in the ***boiler***. Addition of the derivative to the steam and return lines is generally less of a problem because the temperatures are higher.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the synergistic interaction between DEHA and Mimosa tannin.

FIG. 2 illustrates the synergistic interaction between NIPHA and Mimosa tannin.

FIG. 3 shows that Mimosa tannin is more effective than tannin derived from chestnut and from quebracho as an activator for DEHA.

FIG. 4 illustrates the effectiveness of Mimosa tannin with various blends of NIPHA and DEHA using 20% by weight of DEHA and 1% by weight of activator.

FIGS. 5-7 illustrate oxygen removal rates for various combinations of a synthetic tannin and DEHA.

FIG. 8 illustrates the synergistic effect of combinations of molybdate and DEHA.

FIG. 9 illustrates the synergistic effect of combinations of molybdate and NIPHA.

The present invention is based on the surprising finding that the oxygen scavenging activity of hydroxylamine and its derivatives can be catalysed by the presence of small amounts of a tannin. Accordingly the present invention provides a method for the treatment of an aqueous system which comprises incorporating in the system a hydroxylamine derivative of the general formula: ##STR2## wherein each of R.sub.1, R.sub.2 and R.sub.3 which may be the same or different, represents hydrogen, alkyl of 1 to 8 carbon atoms or aryl such as hydrogen, ethyl, isopropyl, phenyl, benzyl or tolyl, or a water soluble salt thereof such as a chloride, sulphate, acid sulphate, phosphate or sulphite, or a precursor thereof and a tannin in a weight ratio of at least 2:1.

Preferred hydroxylamine derivatives include those in which at least one of R.sub.1, R.sub.2 and R.sub.3 represents hydrogen, ethyl or isopropyl. Specific preferred compounds include hydroxylamine, N,N-diethylhydroxylamine (DEHA) and N-isopropyl hydroxylamine (NIPHA). These compounds have the ability to passivate a ***boiler*** metal; it is believed that they do so by generating magnetite. In some circumstances it can be advantageous to use a mixture of hydroxylamine derivatives, typically a mixture of DEHA and NIPHA since they complement each other in their activity. Thus the NIPHA or other N-hydrocarbylhydroxylamines scavenge oxygen faster than the DEHA or other N,N-di-hydrocarbylhydroxylamines. As a result it is possible to use less of the tannin activator and the feed line can be scavenged of oxygen by the NIPHA (under relatively mild conditions), leaving most of the DEHA to volatilise in the ***boiler*** and pass through into the steam lines where it can scavenge oxygen. In general the weight ratio of the two types of derivative will be from 7:1 to 1:7, especially 3:1 to 1:3.

By a "precursor" we mean a compound which converts to a hydroxylamine derivative in the system. Typical examples of such precursors include oximes which are converted in the ***boiler*** to hydroxylamine. These will generally have the formula: ##STR3## where R.sub.1 and R.sub.2 are as defined above; specific examples include methylethylketoxime, acetaldoxime, butyraldoxime and propionaldoxime.

Other precursors include the nitrones which generally have the formula: ##STR4## in which R.sub.1 and R.sub.2 each independently represent hydrogen, alkyl of 1 to 8 carbon atoms or aryl and R.sub.3 represents a hydrocarbon group of 1 to 10 carbon atoms such as a saturated or unsaturated aliphatic acyclic or cyclic group, an aryl group or an aralkyl group, or a water soluble salt thereof. Specific examples include formaldehyde isopropylnitrone, formaldehyde ethylnitrone, acetaldehyde isopropylnitrone, acetaldehyde ethylnitrone, acetone isopropylnitrone and acetone ethylnitrone. Further details of the use of such nitrones can be found in EP-A-283243, to which reference should be made for further details.

References hereafter to hydroxylamine derivatives should therefore be interpreted as including the precursors as well.

Tannins are a large group of water-soluble, complex organic compounds which can be obtained from the various wood and vegetation materials found throughout the world. Almost every tree or shrub that grows contains some tannins in the leaves, twigs, barks, wood or fruit. Examples of barks are wattle (or mimosa), mangrove, oak, eucalyptus, hemlock, pine, larch and willow. Examples of woods are quebracho, chestnut, oak and urunday. Examples of fruits are myrobalans, valonia, divi-divi, tara and algarrobilla. Examples of leaves are sumac and gambier and examples of roots are canaigre and palmetto. Among the preferred materials is the quebracho wood. A spray-dried quebracho powder is commercially available.

These natural tannins can be categorised into the traditional "hydrolyzable" tannins and "condensed tannins" as disclosed by A. Pizzi in "Condensed Tannins for Adhesives", Ind. Eng. Chem. Prod. Res. Dev.

1982, 21, 359-369. Condensed tannin extracts include those manufactured from the bark of the black wattle tree (or mimosa tannin of commerce), from the wood of the quebracho tree (Spanish: Quebra haca, axe-breaker,) from the bark of the hemlock tree, and from the bark of several commonly used pine species. The preparation of wattle (mimosa) and quebracho extracts is a well established industrial practice and such extracts are freely available in considerable amounts, as are extracts from chestnut.

While hydrolyzable tannins are generally mixtures of simple phenols and esters of a sugar, condensed tannin extracts, such as wattle and quebracho, are composed of approximately 70% polyphenolic tannins, 20% to 25% non-tannins, mainly simple sugars and polymeric carbohydrates (hydrocolloid gums), the latter of which usually constitute 3% to 6% of the extract and heavily contribute to extract viscosity, while the balance is accounted for by a low percentage of moisture. Although the exact structure is not known, it is believed that the main polyphenolic pattern in quebracho tannins is represented by flavenoid analogues based on resorcinol A and pyrogallol B rings as shown in formula 1 below: ##STR5## Preferred tannins for use in the present invention are those derived from mimosa, chestnut and quebracho with tannins derived from mimosa being most preferred.

It will be understood that the natural tannin may be replaced in whole or in part by a synthetic tannin or tannin derivative, in particular synthetic tannins whose structure contains functionalities of phloroglucinol, resorcinol, catechol and pyrogallol, for example Resorcinex 9901L obtainable from Advance Resin Systems. Sulphonated synthetic tannins have been found to be particularly effective. Sulphonated Resorcinex 9901 L is believed to have the structure: ##STR6##

In this connection it should be stated that the use of sulphonated tannins in the control of corrosion is believed to be novel and this, i.e. without the necessity of using a hydroxylamine as well, forms another aspect of the present invention.

While it is known that tannins have some ability to prevent corrosion of yellow metal such as copper (various vegetable tannins can absorb oxygen and react with iron to form a protective iron tannate film), it is surprising that they have a catalytic effect on the action of the hydroxylamines to eliminate oxygen. Thus the use of the combination of hydroxylamine derivative and tannin results in faster scavenging and is effective at signficantly lower temperatures than the use of hydroxylamine derivatives alone. While it is possible to incorporate the derivatives separately it is generally more convenient to add them together. Accordingly, the present invention also provides a composition suitable for addition to an aqueous system which comprises a hydroxylamine derivative having the general formula defined above or a water soluble salt thereof or a precursor thereof and a tannin.

The amounts of hydroxylamine derivative used in the present invention will depend on the amount of dissolved oxygen in the system. In general 1 to 70 parts of hydroxylamine derivative are used per part of oxygen, more particularly to 2 to 20 parts. Preferred amounts are about 4 parts in the case of DEHA and 7 parts in the case of NIPHA.

The weight ratio of hydroxylamine derivative to tannin will in general be from 2:1 to 200:1, preferably 2:1 to 40:1 and especially 3:1 to 20:1. The preferred weight ratio is about 4:1.

In the formulation the amount of hydroxylamine derivative will generally be from 5 to 50% by weight, especially 10 to 30% by weight and more especially 15 to 25% by weight, with corresponding concentrations of the tannin. With the preferred ratio the most preferred composition contains about 20% by weight of hydroxylamine derivative and about 5 weight % of tannin.

It will be appreciated that the compositions will normally take the form of aqueous solutions.

The method of the present invention is particularly useful for dosing feed lines where the temperatures are relatively low, typically from 5.degree. to 120.degree. C., generally from 15.degree. to 80.degree. C., and especially from 20.degree. to 75.degree. C. The products can, though, also be added directly to the ***boiler*** or to the condensate and return lines although the effectiveness varies with the precise hydroxylamine derivative employed. In particular DEHA can be used in the condensate lines having volatilised in the ***boiler***. On the other hand NIPHA will tend to decompose more readily in the ***boiler*** and it will not, therefore, generally be useful to add NIPHA and tannin to the ***boiler***.

It will be appreciated that the ***boiler*** water systems can also have included small amounts of additives normally used for the control of corrosion, scaling, sedimentation, and hardeners as well as pH control. In connection with the latter the ***boiler*** water will normally be kept at a pH from 8 to 13 while the pH of the feed will generally be from 7 to 10.5 and more particularly from 8.5 to 9.5. In fact it has been found that a high pH results in a faster oxygen removal rate. A pH of 8 to 12 is generally preferred in the ***boiler***. Particular additives which may be included to advantage are neutralising amines; typical examples of these are ***cyclohexylamine,*** butanolamine, morpholine, monoethanolamine, dimethylaminothanol, methoxypropylamine and dimethylaminopropylamine. Other useful additives include the molybdates, such as sodium molybdate.

Indeed it has also been found that the combination of hydroxylamine derivative (as defined above) and molybdate is synergistic and this forms another aspect of the present invention.

The further Examples further illustrate the present invention:

EXAMPLES

The following tests carried out on a laboratory recirculating rig illustrate the very good oxygen scavenging, and hence oxygen corrosion inhibition, which can be obtained using a blend of hydroxylamine derivative and tannin.

Test Conditions	
System water	Demineralised water
pH	10.5
Temperature	50.degree. C.
Flow rate of water past probe head	200 mls/min
Stirring rate	400 revs/min
Duration of test	120 secs
Concentration of oxygen scavenger in reaction flask	50 ppm Active (DEHA or NIPHA)
Concentration of activator in reaction flask	12.5 ppm Active (MIMOSA Tannin)
Total blend concentration in reaction flask	62.5 ppm Active (DEHA or NIPHA + Mimosa Tannin)

FIGS. 1 and 2 illustrate the synergism that exists between oxygen scavenger and activator. FIG. 3 shows that Mimosa tannin is more effective than tannin derived from chestnut and from quebracho as an activator for DEHA. FIG. 4 illustrates the effectiveness of Mimosa tannin in various blends of NIPHA with DEHA using 20% by weight of DEHA and 1 % by weight of activator. FIGS. 3 and 4 illustrate the % oxygen remaining after 45 seconds.

In further experiments using a different laboratory rig, oxygen removal rates were examined for various combinations of Resorcinex-9901L and DEHA. This involved demineralised water saturated with air for 10 minutes to an oxygen concentration of about 8.3 ppm. The pH was then adjusted as required with sodium hydroxide solution and the additives incorporated with subsequent readjustment of the pH if necessary. The results obtained are shown in FIG. 5. It can be seen that the best results were obtained with a 50:50 mixture. FIGS. 8 and 9 show the synergistic effect of combinations of molybdate (sodium molybdate) and DEHA or NIPHA. The effectiveness of using Resorcinex 9901L without DEHA can also be seen i.e. sulphonated tannins are effective oxygen scavengers.

At pH 11.0 Resorcinex 9901 L/DEHA at 50/50 ratio shows lower initial scavenging rate compared to that of DEHA/HQ at 90/10 ratio. However, the remaining oxygen levels drop to the same level at 160 seconds for these two treatments. Considering the fact that chemicals increase their activities at higher temperature, applying Resorcinex 9901L/DEHA at ***boiler*** temperature might exhibit a much more satisfactory oxygen scavenging rate, i.e., its activity could approach the activity of DEHA/HQ.

Works done at pH 10.0 and 8.50 also demonstrate the synergistic nature of these two chemicals. As shown in FIG. 6, the maximum performance is achieved at a 3:1 Resorcinex 9901L to DEHA ratio at pH 10.0, while FIG. 7 shows the best performance is achieved at a 1:1 Resorcinex 9901L to DEHA ratio at pH 8.50. It is obvious that mixing Resorcinex 9901L with DEHA as a 50/50 mixture results in highest activity.

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Moran, P.J. and P.M. Natishan 1993

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Corrosion-Resistant Materials

Alloys having varying degrees of corrosion resistance have been developed in response to various environmental needs. At the lower end of the alloying scale are the low alloy steels. These are iron-base alloys containing from 0.5–3.0 wt % Ni, Cr, Mo, or Cu and controlled amounts of P, N, and S. The exact composition varies with the manufacturer. The corrosion resistance of the alloy is based on the protective nature of the surface film, which in turn is based on the physical and chemical properties of the oxide film. As a rule, this alloying reduces the rate of corrosion by 50% over the first few years of atmosphere exposure. Low alloy steels have been used outdoors with protection.

The stainless steels contain appreciable amounts of Cr, Ni, or both. The straight chrome steels, types 410, 416, and 430, contain about 12, 13, and 16 wt % Cr respectively. The chrome–nickel steels include type 301 (18 wt % Cr and 9 wt % Ni), type 304 (19 wt % Cr and 10 wt % Ni), and type 316 (19 wt % Cr and 12 wt % Ni). Additionally, type 316 contains 2–3 wt % Mo which greatly improves resistance to crevice corrosion in seawater as well as general corrosion resistance. All of the stainless steels offer exceptional improvement in atmospheric conditions. The corrosion resistance results from the formation of a passive film and, for this reason, these materials are susceptible to pitting corrosion and to crevice corrosion. For example, type 304 stainless has very good resistance to moving seawater but does pit in stagnant seawater.

Several copper alloys are exceptionally resistant to certain atmospheres. The copper–nickel alloys, 90% Cu–10% Ni and 70% Cu–30% Ni, have very good resistance to corrosion in seawater, if the iron content is properly controlled, ie, from 0.5 to 1% Fe. Because of the high copper content, these alloys also resist macrobiological fouling as well as corrosion in most aqueous environments. Monel alloy (66.5 wt % Ni–31.5 wt % Cu) is widely used in marine service where strength is also required. Several copper alloys, silicon bronzes, aluminum bronzes, and manganese bronzes are resistant to severe atmospheric corrosion conditions, and because of their high strength are used as bolts, clamps, or load carrying parts in outdoor environments. Specific alloys have been found suitable for very corrosive environments. For example, Carpenter 20, which is 20 wt % Cr–29 wt % Ni–2.5 wt % Mo–3.5 wt % Cu, has outstanding resistance to concentrated sulfuric acid.

For most environments quantitative studies have been reported describing the corrosion rate of various materials including a number of corrosion-resistant alloys (30). For example, Table 4 gives weight losses suffered by corrosion-resistant alloys in a solution of 28% phosphoric acid [*7664-38-2*], 20–22% sulfuric acid [*7664-93-9*], and 1–15% fluoride (36).

Inhibitors

Corrosion inhibitors are substances which slow down or prevent corrosion when added to an environment in which a metal usually corrodes. Corrosion inhibitors are usually added to a system in small amounts either continuously or intermittently. The effectiveness of corrosion inhibitors is partly dependent on the metals or alloys to be protected as well as the severity of the environment. For example,

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Table 4. Plant Corrosion Test in Sulfuric Acid Dilution with Recirculated Phosphoric Acid[a]

Material	Corrosion rate, μm/yr	Concentration cell depth, μm
Carpenter stainless no. 20Cb	28	
Aloyco 20	38	
Incoloy alloy 825	69	127
Hastelloy alloy C	71	
Illium "G"	76	
Inconel alloy 718[b]	81[c]	
Worthite	109	76
Incoloy alloy 901[d]	155	127
Illium "R"	175, 363	
Monel alloy K-500[e]	787	[f]
Monel alloy 400	965	
Hastelloy alloy B	1980	
stainless type 317	>3800	
stainless type 316	>4600	

[a] Phosphoric acid (wet-process) 28% (20% P_2O_5), sulfuric acid 20–22%, fluoride approx 1–1.5%, probably as hydrofluosilicic acid; temperature 82–110°C, average 93°C; and duration of test 42 days, moderate aeration, agitation by convection only.

[b] Composition 52.5% Ni, 18.6% Cr, 18.5% Fe, 5.0% Nb, and 3.1% Mo.

[c] Pitted to a maximum depth of 127 μm.

[d] Composition 42.7% Ni, 34.0% Fe, 13.5% Cr, 6.2% Mo, and 2.5% Ti.

[e] Composition 65.0% Ni, 29.5% Cu, 2.8% Al, and 1.0% Fe.

[f] Pitted to a maximum depth of 76 μm.

the main factors which must be considered before application of a corrosion inhibitor to an aqueous system are the compatibility of the inhibitor and the metal(s), the salt concentration, the pH, the dissolved oxygen concentration, and the concentration of interfering species such as chlorides or metal cations. In addition, many inhibitors, most notably chromates, are toxic and environmental regulations limit use. Attention is now being given to the development of more environmentally compatible inhibitors (37).

Inhibitors act and are classified in a variety of ways (1,3,37,38). The classifications used herein closely follow the discussion in Reference 37. Types of inhibitors include: (*1*) anodic, (*2*) cathodic, (*3*) organic, (*4*) precipitation, and (*5*) vapor-phase inhibitors.

Anodic Inhibitors. Passivating or anodic inhibitors produce a large positive shift in the corrosion potential of a metal. There are two classes of anodic inhibitors which are used for metals and alloys where the anodic shift in potential promotes passivation, ie, anodic protection. The first class includes oxidizing anions that can passivate a metal in the absence of oxygen. Chromate is a classical example of an oxidizing anodic inhibitor for the passivation of steels.

The second class of anodic inhibitors contains ions which need oxygen to passivate a metal. Tungstate and molybdate, for example, require the presence of oxygen to passivate a steel. The concentration of the anodic inhibitor is critical for corrosion protection. Insufficient concentrations can lead to pitting corrosion or an increase in the corrosion rate. The use of anodic inhibitors is more difficult to maintain the volatile compound, but objects as large as the interior of an oceangoing tanker have been treated by this technique.

Coatings for Corrosion Prevention

Coatings (qv) are applied to metal substrates to prevent corrosion. Generally the coating protects the metal by imposing a physical barrier between the metal substrate and the environment. However, the coating can also act to provide corrosion protected by cathodic protection or by serving as holding reservoirs for inhibitors. Coatings may be divided into organic, inorganic, and metallic coatings (1–3, 39,40). For an in-depth coverage of this topic see References 1–3 (see also COATINGS, MARINE; METAL SURFACE TREATMENTS).

Coating Types. Organic coatings afford protection by providing a physical barrier and are often used as holding reservoirs for corrosion inhibitors. Organic coatings include paints, resins, lacquers, and varnishes (see also BARRIER POLYMERS; PAINT). These coatings probably protect more metal on a tonnage basis than any other means of corrosion protection. As a rule, however, organic coatings should not be used in environments that would rapidly corrode the metal if the coating were compromised. For example, paint would not be used to protect the inside of a tank car used for shipping hydrochloric acid because one small coating defect would result in the rapid perforation of the tank car wall. The effective application of an organic coating requires: (*1*) proper surface preparation of the metal substrate, (*2*) selection of the proper primer, and (*3*) selection of the appropriate top coat(s). Poor performance of organic coatings most often results from improper surface preparation or poor application (1). Maintenance programs involving periodic inspection and repair are necessary for reliable corrosion protection by organic coatings.

Inorganic coatings are also used to provide a barrier between the environment and the metal (1,2,39). Inorganic coatings include chemical conversion coatings, glass (qv) linings, enamels (see ENAMELS, PORCELAIN OR VITREOUS), and cement (qv). Chemical conversion coatings are produced by intentionally corroding the metal surface in a controlled manner. This is done so as to produce an adherent corrosion product that protects the metal from further corrosion. Anodization of aluminum produces a protective aluminum oxide film on the aluminum metal. Other examples of chemical conversion coatings include phosphatizing for the protection of automobile bodies and chromatizing for the protection of zinc and magnesium. Porcelain enamel coatings which are inert in water and resistant to most weather are routinely applied to steel, cast iron, and aluminum. They are commonly seen on appliances and plumbing fixtures. Glass-lined metals are used in process industries where there is concern over corrosion or contamination of the product. Glass-lined steels are used in the pharmaceutical industry, breweries, and food plants. Portland cement coatings have been used to protect steel and cast-iron water pipes and have an excellent performance record.

In some cases, metallic coatings, in addition to providing a barrier between the metal substrate and the environment, provide cathodic protection when the coating is compromised (1,3,40). Metallic coatings (qv) are produced using techat higher salt concentrations, higher temperatures, lower pH values, and in some cases, at lower oxygen concentrations (37).

Cathodic Inhibitors. Cathodic inhibitors act to retard or poison the cathodic reaction or selectively precipitate onto cathodic areas producing diffusion barriers to cathodic reactants, thereby reducing the rate of the cathodic reaction. There are three types of cathodic inhibitors: (*1*) hydrogen poisons, (*2*) oxygen scavengers, and (*3*) cathodic precipitates. Hydrogen poisons are chemical species such as arsenic or antimony that retard the hydrogen reduction reaction. Because the hydrogen poison slows the cathodic reaction, and because the cathodic and anodic reactions must proceed at the same rate, the whole of the corrosion process is slowed. A potentially serious drawback upon use of hydrogen poisons is that the hydrogen on the surface can be more easily absorbed into the metal or alloy and can lead to HIC in susceptible materials.

Oxygen scavengers prevent corrosion by tying up the oxygen in solution, thereby making it unavailable for the cathodic reaction. The most common oxygen scavengers used in water at ambient temperatures are sulfur dioxide [*7446-09-5*] and sodium sulfate [*7757-82-6*]. Cathodic precipitate inhibitors such as calcium carbonate [*471-34-1*] or magnesium carbonate [*546-93-0*] precipitate onto the cathodic areas producing a film that reduces the cathodic activity (37).

Organic Inhibitors. Generally, organic inhibitors adsorb on the entire metal surface and impede corrosion reactions (37). Organic inhibitors consist of broad classes of organic compounds. For example, aliphatic organic amines (qv) adsorb by the surface-active $-NH_2$ group which forms a chemisorptive bond with the metal surface. The hydrocarbon tails orient away from the interface toward the solution, so that further protection is provided by the formation of a hydrophobic network which excludes water and aggressive ions from the metal surface (38). Organic inhibitors influence both anodic and cathodic reactions to varying degrees depending on the potential, the chemical structure of the inhibitor, and the size of the inhibitor molecule. Soluble organic inhibitors produce a protective layer that is only a few molecules thick, whereas insoluble inhibitors added as dispersions can build a film to a thickness of several hundredths of a centimeter (37).

Precipitation and Vapor-Phase Inhibitors. Precipitation inhibitors are film-forming compounds that produce barrier films over the entire surface. Phosphates and silicates, which are the most common, do not provide the degree of protection afforded by chromate inhibitors, but are useful in situations where nontoxic additives are required. Two main drawbacks to the use of phosphates and silicates are the dependence on the water composition and the control required to achieve maximum inhibition (37,38).

Vapor-phase inhibitors are volatile compounds that adsorb onto metal surfaces, and retard or prevent corrosion by a variety of mechanisms (37). Inhibitors such as dicyclohexamine nitrate [*3882-06-02*] can protect a variety of metals such as steel, aluminum, and tinplate. A number of vapor-phase inhibitors are commercially available as powders or tablets. However, vapor-phase inhibitors attack nonferrous metals to varying degrees, thus the manufacturers' recommendations should be checked before application. The system to be protected must be closed

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Coatings

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niques such as hot dipping, electroplating, cladding, flamespraying, chemical vapor deposition, or by surface modification using directed energy (laser or ion) beams.

Coating Techniques. Hot dipping is one of the oldest methods used for coating metals. In hot dipping, coatings are applied by dipping the metal in a molten bath commonly of zinc, tin, lead, or aluminum. The best known hot dipping procedure is that of coating steel with zinc to produce galvanized steel. In addition to providing a barrier between the steel substrate and the environment, the zinc acts as a sacrificial anode and provides cathodic protection to the underlying steel when the coating is breached.

Electroplating (qv) consists of immersing a metal in a plating bath and electrochemically plating the solution species onto the metal substrate. Additives to the plating bath can improve coating properties such as grain size, strength, uniformity, and brightness. The electroplate can be a single metal, an alloy, or a sequence of layers of different composition. Coating thicknesses can range from a few hundredths of a micrometer to upward of 500 μm. Zinc, nickel, tin, and cadmium are the most commonly plated materials on a tonnage basis. Electroplated tin is used as a protective coating for food cans (see FOOD PACKAGING). The electroplated tin provides a physical barrier and galvanic protection if the coating is compromised. However, the tin coating cannot provide galvanic protection in the presence of dissolved oxygen so that food should not remain in tin plated cans after opening.

The ability to modify metal surfaces using directed energy beams is providing a new flexibility in attempting to improve the corrosion resistance of metals. Techniques such as ion implantation (qv), ion beam mixing, and ion beam assisted deposition (IBAD), as well as laser-surface alloying and processing have been used to improve the corrosion behavior of metals (see LASERS). These techniques are versatile and have been used to modify the cathodic or anodic reactions, improve the nature of passive films, and produce a barrier coating (40). Ion implantation has been used to improve the corrosion resistance of titanium in hot acids and aluminum and steels in aqueous chloride environments (40).

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55 What is reverse osmosis?

ANSWER: This term is often applied to the membrane process of water ineralizing. The physical phenomena of *osmosis* reveals that if pure wat separated from a solution with impurities by a partition such as a memb with no pressure applied, then the pure water will slowly flow through partition into the solution containing the impurities.

In *reverse osmosis,* pressure is applied on the solution side with the impu ties so that the flow of purer water through the membrane is reversed, he the term *reverse osmosis.*

Kohan, A.L. 1997
New York: McGraw-Hill

Chapter

13

Boiler Water Problems and Treatment

Standard water testing and treatment specification is more and more being performed by water treatment specialty companies working with boiler plant operators. There is a complementary role for both in solving boiler water effect problems so that the boiler can be operated safely, efficiently, and continuously as needed.

Boiler water problems can cause scale, corrosion, priming and foaming, carryover, stress-corrosion, and embrittlement in the boiler or connected steam-using machinery, such as steam turbogenerators. Many steam turbine blade failures can be traced to steam conditions. As a result, there has been a continuous tightening of permissible concentrations of impurities in steam going to the steam turbine, and this has caused a general improvement in water chemistry as applied to boilers. There are also technological changes being made as research develops new and better chemicals for eliminating the objectionable concentrations of impurities in boiler water. This means operators must be alert to the various methods that are now or will become available in solving boiler water problems.

Basic Water Chemical Characteristics

Definitions applicable to water chemistry:

1. *Acid:* A compound that yields hydrogen ions, such as sulfuric acid.
2. *Alkali:* A substance or salt that will neutralize an acid.
3. *Base:* A compound which can react with acids to form a salt and in water solutions yields hydroxyl ions.

4. *Colloidal:* A gelatinlike substance which appears to be in a dis solved state but is actually in suspension. It is made of very ti particles.

5. *Concentration:* This is applicable to solutions and expresses th ratio of the dissolved substance to the amount of water, usual expressed in a weight ratio.

6. *Corrosion:* The chemical action of a metal being combined form an oxide of the metal by the action of oxygen, an acid, alkali on the metal.

7. *Grain:* A unit of weight as used in water treatment, with 700 gr equaling 1 lb.

8. *Hardness:* A measurement of the amounts of calcium and ma nesium compounds in solution in water because the chemic action of these compounds forms an insoluble product, or scale the water.

9. *Hydrogen ion:* An ion formed from hydrogen with the sym H^-, which forms an acid when combining with certain impuriti in water.

10. *Hydroxyl ion:* This has the symbol OH^- and forms a base com pound when combined with some impurities in water.

11. *Ionization of water:* The breaking up of a molecule of water in hydrogen ions and hydroxyl ions with the reaction proceeding a higher rate at higher water temperature.

12. *Oxide:* The chemical combination of oxygen with a meta form the metal oxide, such as iron oxide, commonly called rus

13. *Parts per million, or ppm,* is a measure of the amount of impu ties on a weight basis to one million pounds of water. Also us *grains per gallon* = 17.1 ppm; *milligrams per liter* or mg/L.

14. *pH:* A measurement of the hydrogen-ion concentration in or to measure the relative acidity or alkalinity of a solution. It is logarithm to the base 10 of the reciprocal of the hydrogen concentration, with 7 being neutral. Below 7, the solutio acidic; above 7, it is base.

15. *Precipitate:* The solid substance that is separated from a so tion by chemical reaction in the solution.

16. *Reagent:* A substance of a known strength which is used fo detection and measurement of another unknown substance.

17. *Salts:* Those substances which in solution yield ions other hydrogen or hydroxyl. They are also the product of an acid base combining or an acid and certain metals chemically reacting.

Scale: An adherent deposit on metal surfaces in a boiler, which is caused primarily by impurities precipitating out of the water and cementing on the metal as temperatures rise in the boiler.

Soluble: The ability of a substance to go into solution by dissolving.

Condensate: Steam that is condensed in the steam loop and is returned to the boiler system.

Makeup water: Water that must be replenished in the boiler system as a result of leakage, blowdown, and steam process use.

Feedwater: The combination of condensate and makeup water that is supplied to the boiler for evaporation.

Blowdown: The bleeding of a portion of the water in the boiler in order to remove suspended solids.

Condensate polishing: The purification of returned condensate by passing it through demineralizers.

The treatment of boiler water is a problem requiring periodic test- of the water and proportioning the treatment according to the ying conditions. There are a number of reputable laboratories pre- red to equip small or large plants with suitable test kits and to sup- or advise the proper treatment indicated by the tests.

Chemical tests. Minimum chemical tests usually prescribed for h-pressure boilers are dependent on ratio of makeup water to con- sate making up the boiler feedwater as well as with the treatment ed or specified by water-treatment specialists. For information pur- es, here are some tests and their purpose:

Acidity or alkalinity test: This is used for controlling corrosion and also scale by using the values obtained in calculating the amount of alkali to be added to an acidic raw water, or the quanti- y of lime and soda that may be needed in a lime-soda water soft- ener.

Testing for hardness, calcium, and magnesium: A measurement of calcium and magnesium is a measure of the hardness of raw and softened waters and feedwaters. Hardness produces scale in a boiler, therefore the values obtained for calcium and magnesium can be used to determine the quantity of lime and soda ash that needs to be added to the boiler water, and thus control scale forma- tion.

ing. However, feedwater must have low hardness, of less than 2 p for this treatment to be economical. This makes its use limited to so ened or demineralized makeup water. The two commonly used chela ing agents are EDTA (ethylenediaminetetraacetic acid), and NT (nitrilotriacetic acid). Both agents form stable salts with calcium an magnesium. However, it requires 10 ppm of EDTA and 5 ppm of NT to tie up each 1 ppm of hardness. This makes the treatment expen sive, so it is mostly applied to low hardness pretreated feedwat Another problem is that EDTA starts to break down at 300 psi, and a about 1500 psi it loses its ability to chelate. NTA loses its chelatin ability at about 900 psi. Thermal degradation makes it impractical t monitor the free chelant residuals in boiler water, which makes co trol of dosages difficult. Chelants themselves can cause corrosion i the boiler if overfeed of the chelant occurs for any lengthy period o time.

Below 400 psi, another group of chelating-type chemicals are use termed *organic phophonates* with the abbreviated terms AM (aminomethylene phosphonate), and HEDP (hydroxethyliden which have the property of inhibiting calcium carbonate scale. All so ubilizing agents show capability similar to EDTA and NTA for kee ing calcium and iron in solution, but are not as strong, and therefo do not pose as great a threat as chelants for causing corrosion attac The phosphonates can be used more economically than the chelan at feedwater levels of 50 ppm and higher.

Polymer or sludge conditioning. In industrial boilers, the carbona cycle of scale control involves the intentional precipitation of calciu hardness salts as calcium carbonate with polymer additions to pr vide a conditioned sludge. Anionic polymers are widely used in indu trial boilers where the polymer molecules wrap themselves aroun suspended boiler sludge. This introduces to the sludge a degree of di persancy, or fluidity, which permits easier removal of sludge by bo tom blowdown. There are various synthetic polymers sold by wat treatment companies. For example, Nalco Chemical Co. uses th name Transport-plus for its polymers. It is applied to boilers up t 1500 psi, and the term "transport" is used to indicate that it ca transport virtually 100 percent of feedwater impurities, includin hardness, silica and iron impurities, through the boiler syste because the polymer makes the sludge more fluid for eventual blo down control. The anionic polymers inhibit growth of the crystal-la tice structure of scale. This process also weakens the scale as th polymer becomes absorbed in the scale structure, and smaller par cles of scale are formed as a result.

Control of the feed rate and polymer depends on the test metho used to check on concentrations. Overtreatment is still a thre

tes and polymethacrylates as the major components of a blended olymer treatment program.

il deposits

il in boilers is a dangerous condition. Oil is an excellent heat insula- or, and its presence on heating surfaces exposed to high tempera- res may cause serious overheating and damage to the boiler.

A common cause of this condition was the use of reciprocating team-equipment exhaust containing cylinder oil for condensate eturn to the boiler feed system. Also, fuel-oil heating equipment may eak oil into the steam system and cause this difficulty if the conden- ate is returned to the boiler. A minimum amount of high-grade prop- rly compounded cylinder oil should be used for lubrication of steam ngines and pumps where condensate is returned, and an efficient ype of oil separator should be used in the exhaust system. Oil may lso enter the feed through its presence in such raw-water supplies as vers and streams contaminated by mill, marine, or trade wastes.

Scale and oil removal. Water-side *scale removal* is accomplished by e of three methods: mechanical removal, water treatment, and acid eaning. Mechanical removal of scale is effected while the boiler is le and empty. The accessible parts of shells, drums, heads, and aces are chipped with a dull chisel or scaling hammer, care being ken not to score the metal. Scale may be ground off the internal rfaces of water tubes with a tube turbine. Water is generally used o wash out ground "scale sludge" while the tube turbine is in opera- on. Care should be exercised not to operate a tube turbine too long n one place or to force it unduly, for damage to the tube may thus sult.

Extreme care should be taken in removing existing scale in a boiler y treatment of the water. If the scale is removed too quickly, it may rop down in large quantities, with serious damage to the boiler eing the result because of restricted circulation and overheating. In watertube boiler, ruptured tubes may be the consequence; in a fire- be boiler, bulges and even rupture in the shell have followed.

Scale deposits on external surfaces of fire tubes may be vibrated oose with a tube rattler or by shaking a long, heavy bar in each tube. xtreme care should be taken after such mechanical treatment to see at *all* loosened scale is removed from the boiler before closing it up r operation. Many cases of serious damage have resulted from loose ale accumulations left in boilers. See Fig. 13.6.

Acid cleaning of boilers is often used to remove metallic oxide. The lvents used for acid cleaning are varied. Some use hydrochloric acid;

Figure 13.6 Collapsed scotch marine boiler's corrugated furnace caused by scale and dry firing. (*Courtesy Royal Insurance Co.*)

others, phosphoric acid. The usual procedure is to fill the boiler until the solution overflows at the air vent (acid is added outside the boiler). The solution is *allowed* to soak the boiler from 4 to 6 hr, followed by refilling with a neutralizing agent. If hydrochloric acid is used for soaking, a weak solution of phosphoric acid is used. After draining, fresh warm water is used for flushing; then the boiler is immediately filled with an alkaline solution and boiled again for several hours. This solution is drained; the boiler is flushed again and then refilled with normal service water, with proper feedwater treatment started immediately.

A precaution to be observed in acid cleaning of boilers equipped with a superheater and other such bent tubes is to make sure all traces of acid are thoroughly cleaned out of U bends. This is critical in the neutralizing and flushing stage after the tubes are soaked with an acid solution. Compressed air may have to be used to force the solution out of dead pockets. If this is not done, the acid solution may not be completely cleared, and thinning of tubes will result. Acid cleaning of older riveted boilers can be dangerous because the acid may settle under the butt straps or lapped plates and eat up these holding elements. Thus riveted boilers are usually not acid-cleaned.

Areas subject to high local stress and repetitive application of stress may be affected by acid treatment. Tubes that have been repeatedly rolled and acid-cleaned may develop tube-roll leakage. T with further rolling impossible, new tubes may be required.

the prevention of scale in a boiler is still the best method of keeping a

To guard against the consequences of superheater chemical contamination, one of the most important practices prior to proceeding with a chemical cleaning operation is to carefully review the entire piping arrangement and procedures. All the cognizant personnel involved in the chemical cleaning must be familiar with the cleaning method and flow paths to be used in filling, draining, adding chemicals, backfilling the superheater, etc. All possible paths (such as drain lines from the superheater connected with lines or manifolds being used for filling or draining the boiler) should be examined closely to ensure that cleaning solutions being fed to or drained from the boiler do not have a possible flow path to the superheater. The lines used to fill the superheater with water during the boiler cleaning should preferably not be connected with boiler chemical fill or drain lines. If flow paths exist between the superheater and the boiler fill or drain lines or manifolds, positive means of isolation must be provided. Double valves with a telltale connection between them are the minimum recommendation.

Caustic soda and soda ash are the old standbys for cleaning oil from the water side of boilers. One pound of each chemical is added for every 1000 lb of water required to fill the unit. After the boiler is filled with water, drum vents open, and a light fire is started and maintained until the vents issue steam. After the vents are closed, pressure is built up to 25 psig and held while boiling for 24 hr. Some operators blow down to half a gauge glass after about 4 hr of boiling. But 24 hr after boiling, the solution is dumped, and the unit is refilled with fresh hot water with the vents open. After this, flushing water is dumped and a thorough internal inspection is made. If necessary, a hose is used for spraying hot water for final cleaning.

Water treatment specialists also recommend the following if small amounts of oil entering the boiler water is a continual problem: (1) For free oil in the water going to the boiler, use the flotation method to separate out the oil from the water, as described in previous chapter; (2) For oil that is emulsified, use special chemicals prescribed by the treatment company to break up the emulsion, then filter the water with special leaf-type filters, assisted by diatomaceous earth.

Corrosion and Its Effects

Corrosion is the second cause of boiler water problems after scale formation. While there are many causes of corrosion in boiler water, including chemical reactions from wrong dosages of chemicals, the causes of corrosion can be grouped together by their attack on the boiler metal. Corrosion in boilers is the deterioration metal by chemical reaction. The metal is dissolved or eaten away. The corrosive effect can seriously weaken the metal so that unexpected failure o pressure-containing part of the boiler can occur. This section wi review the principal causes of corrosion as:

1. The relative acidity of the boiler water.
2. The presence of dissolved oxygen in the boiler water.
3. Electrolytic action.

Sources of acid. Acidic conditions in boiler water usually resu from chemical reactions and not from direct entrance of an acid fro condensate or feedwater. Acid-forming substances are (1) carbon dio ide gas; (2) magnesium chloride; (3) magnesium sulfate; (4) sodiu chloride; (5) certain oils.

The most important of these is carbon dioxide gas, which is th most soluble of all gases in water and has a tendency to form carbon acid, H_2CO_3. The chemical breakdown of the bicarbonate salts unde heat always liberates carbon dioxide gas, as shown by the following:

$$Ca(HCO_3)_2 + Heat = CaCO_3 + H_2O + CO_2$$

The carbon dioxide continues the chemical reactions by combin with water as follows:

$$CO_2 + H_2O = H_2CO_3$$

The carbonic acid can combine with iron or boiler metal as follows:

$$Fe + H_2CO_3 = FeCO_3 + H_2$$

The ferrous carbonate may combine with water to continue the chem ical reaction as follows:

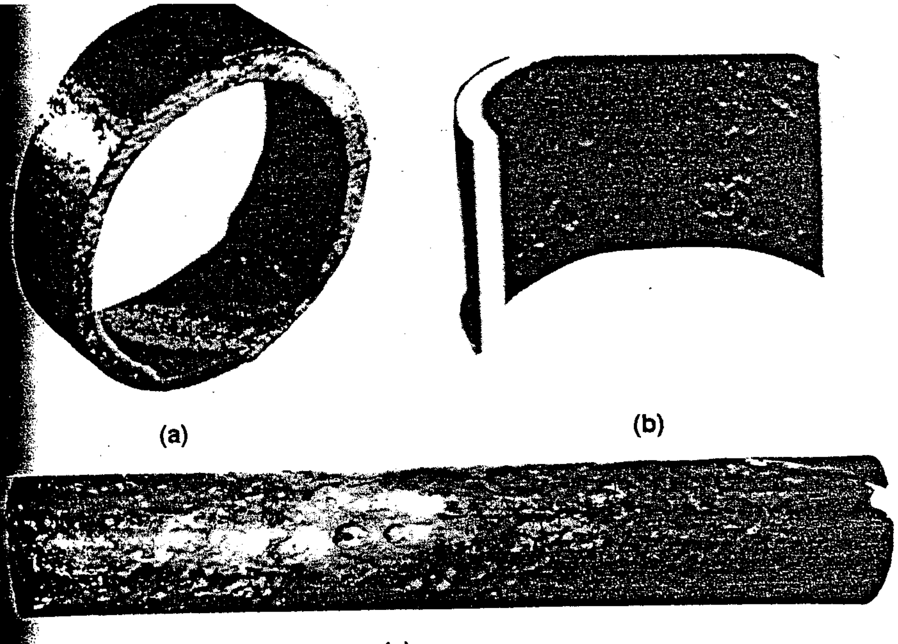
$$FeCO_3 + 2H_2O = Fe(OH)_2 + H_2CO_3$$

Note that carbonic acid was formed again, and this can continue t combine with boiler iron, thus weakening the metal. It also explai why a small amount of acid can continue the corrosion process. Se Fig. 13.7*a*. Magnesium chloride, a component of seawater, can for hydrochloric acid by the following chemical reaction:

$$MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl$$

Magnesium chloride can also be formed by the chemical reaction o sodium chloride salt with magnesium sulfate salt. Both are present i seawater. The reaction is:

$$2NaCl + MgSO_4 = Na_2SO_4 + MgCl_2$$


(a)

(b)

(c)

gure 13.7 Types of boiler metal attacks from water impurities. (*a*) Carbonic acid ack on watertube boiler; (*b*) pitting attack from oxygen in watertube boiler; (*c*) pit- g attack on outside surfaces of firetube boiler tube.

he magnesium chloride will react with boiler water to form ydrochloric acid, HCl, as shown in the previous equation. ydrochloric acid reacts with iron or boiler metal as follows:

$$Fe + 2HCl = FeCl_2 + H_2$$

he iron chloride, $FeCl_2$, can combine with water as follows:

$$FeCl_2 + 2H_2O = Fe(OH)_2 + 2HCl$$

Again, an acid was formed to continue the attack on boiler metal. he entire corrosive action of these acids is due to the behavior of the ydrogen ions they contain. The iron atoms become ions in water lutions. Iron accepts only positively charged ions, which hydrogen as. The hydrogen gives up its charge to the iron, and thus assists it leaving the boiler metal to combine with the acid radical, such as O_3.

Acid corrosion detection, besides visual inspection for corrosion, epends on the various tests that are available when such acidic conditions are present so that the operator, with assistance from water treatment specialists, can take action before serious damage may result. The most often-used tests are the pH and alkalinity tests.

The prevention of acid corrosion depends on keeping the hydrogen ion concentration as low as possible and within certain limits. These limits have been set from experience, so that acid corrosion can be prevented by maintaining a boiler water value above 9.6 on the pH scale, with the usual operating range being between 10.0 and 10.5 pH. Since neutral water has a pH of 7.0, it is necessary to add compounds containing a base or alkaline solution to raise the pH value to the desired level by careful, calculated dosages. The advice of water treatment specialists must be followed as well as the methods of conducting acidity and alkaline tests per the usual instructions provided by chemical suppliers. For example, there are instructions for alkalinity that apply if the indicator solution is phenolphthalein or if the indicator is methyl orange.

Oxygen corrosion

Oxygen causes the corrosion of boiler metal in two ways:

1. The presence of free oxygen in the boiler water results in a pitting attack on the boiler metal as shown in Fig. 13.7*b* and 13.7*c* if it is of a localized area. Oxygen will also unite with the boiler metal in a general way to produce iron oxide (rust). Free oxygen can be produced as the temperature of the boiler water rises, and the oxygen is forced out of the solution. The oxygen then attaches itself in the form of a bubble or gas to a heating surface of the boiler to start the chemical reaction between oxygen and iron. The solubility of oxygen in water varies with the temperature of the water solution; it is generally assumed that oxygen comes out of solution usually above 750°F.

2. The second type of oxygen attack is as a catalyst, where it does not unite with the metal directly, but assists other corrosive elements in the boiler water to react with the metal or speeds up the reaction. This action is related to the exchange of metals by the natural ionization of water into H^+ ions and OH^- ions. Any free oxygen present in the boiler water tends to unite with the hydrogen, which generally is plated out on the metal surfaces. The H^+ ions give up their electrical charge to the iron atoms, allowing them to leave the boiler plate and combine chemically with the hydroxyl ion, OH^-. This produces ferrous hydroxide in the boiler water. Any free oxygen present in the boiler water tends to unite with the hydrogen in the film adhering to the boiler metal, and this forms water. This permits more hydrogen to settl[illegible]n the boiler metal and combine with the boiler metal to form ferr[illegible] hydroxide. Thus, the amount of oxygen present determines the rate of hydroxyl reaction with boiler metal to form ferrous hydrox-

de. The more oxygen present, the more rapidly is the hydrogen film destroyed on the metal, and the greater will be the iron going into solution to form ferrous hydroxide.

Oxygen-type corrosion is prevented (1) externally by the use of deaerators and (2) chemically by the use of oxygen-scavenging chemicals. Chemicals commonly used for this purpose are sodium sulfite, hydrazine, and catalyzed hydrazine.

Sodium sulfite reacts with oxygen to form sodium sulfate as shown by the chemical equation

$$2Na_2SO_3 + O_2 = 2Na_2SO_4$$

Sodium sulfate + oxygen = sodium sulfate

It is generally required to use eight parts of sodium sulfite for each part of dissolved oxygen. Sodium sulfite for the scavenging of oxygen is applied to boilers to about 1800 psi. It is not used above this pressure because thermal decomposition of the sodium sulfite chemical produces acidic gases, SO_2 and H_2S.

Hydrazine reacts with equal parts of oxygen to produce inert nitrogen and water as shown by the equation

$$N_2H_4 + O_2 = N_2 + H_2O$$

Hydrazine + oxygen = nitrogen + water

This chemical reaction produces products that are volatile or neutral, and thus does not increase the dissolved-solids concentration in boiler water. Hydrazine is effective at low levels of application. Since it is highly volatile itself, it may decompose thermally to ammonia and nitrogen as follows:

$$3N_2H_4 + \text{heat} = 4NH_3 + N_2$$

= ammonia + nitrogen

The evolution of ammonia may restrict hydrazine application to preventing an increase in pH above the desired control point. Plants without condensate polishing systems sometimes use hydrazine in condensate based on pH control criteria.

The sluggish reaction of hydrazine with oxygen at low temperatures has resulted in high-pressure plants using this chemical only to scavenge oxygen. This has led to the development of organically catalyzed hydrazine, so that low- and medium-pressure [illegible]ler plants may also use it for oxygen scavenging. These catalysts [illegible] speed up the reactivity. One of the hydrazine catalysts is hydroquinone.

Hydrazine is considered carcinogenic; therefore, protective cloth is required in handling the chemical. Many plants use automatic systems to avoid human contact. This concern has also led to development of substitute scavengers, such as carbohydrazide, thorbic acid, methylethyl ketoxime, and DEHA (diethylhydro amine). Operators must carefully review their application and th effects on the boiler conditions on a case-by-case basis.

In higher-pressure boilers it is also necessary to control boi water *silica concentration* by automatic analysis. Silica is the firme toughest, and most difficult to remove of all the dissolved mine This removal is critical, for silica is apt to carry over with the stea Silica's glasslike deposits inhibit heat transfer, resulting in tu burnout. When deposited on turbine blades, silica will reduce effici cy, which often results in rotor unbalance, necessitating costly a premature shutdowns.

Figure 13.3 provides some boiler and feedwater limits that are r ommended by various authorities. The ASME has published, throu its Committee on Water in Thermal Power Systems, a guide on wa quality for industrial boilers entitled "Consensus on Operat Practices for the Control of Feedwater and Boiler Water Quality Modern Industrial Boilers." This paper should be used as a guide establishing water-quality limits for the boiler size involved.

After-boiler corrosion and treatment. *Condensate returns* are a w of saving fuel; however, condensate also produces water proble The condensate-return system may have corrosion products fro steam and condensate piping, which can form highly insulat deposits on boiler surfaces. Improved steam and return-line corrosi control must be used to limit this sludge. The most common attacke of the condensate systems are dissolved oxygen and carbon dioxi that find their way into the steam system.

The condensate-return system is a very revealing sample point monitor total boiler water-treatment performance. The amount contaminants found, and their nature, will often point out malfun tions and suggest corrective action in the rest of the syste Permissible contaminant levels would depend on the nature of th troublesome constituent, boiler design, and operating pressure Dissolved oxygen and carbon dioxide, for example, can be directly indirectly responsible for many system failures and are often mon tored in condensate.

Carbon dioxide in condensate return systems has receive increased attention because it can form carbonic acid and attack th steel metal of a boiler system. Carbon dioxide is evolved from th breakdown of feedwater bicarbonate and carbonate alkalinity.

Monitoring and control of hardness, conductivity, and specific con

inants (such as iron and copper)

nsate reuse.

Nuclear boiler systems deserve further considerations, for condenete return is usually considered a radioactive substance and requires cial monitoring.

ondensate polishing is the term used for the removal of solid nces as well as dissolved solids that are found in condensate sysms. In the utility field, the two condensate polishing systems used the externally applied precoat filter and the mixed-bed demineralin order to eliminate the solids. Condensate systems also can be mically treated to control corrosion damage caused by water, cardioxide, and oxygen. The treatment chemicals include neutralizamines, filming amines, hydrazine, and sometimes ammonia.

Corrosion in steam lines and return lines is caused primarily from reaction of CO_2 with water to form carbonic acid. The CO_2 may me from condenser or other steam-using equipment that permits to leak into the system at low or vacuum pressure conditions. It also shown that bicarbonate alkalinity can produce CO_2. Buildup acidic conditions will reduce the condensate pH value, and this ults in metal loss in piping and general corrosion. Oxygen present the condensate will accelerate the corrosion.

Two methods are used to combat after-boiler corrosion attack:

Neutralizing amines such as cyclohexylamine, morpholine, and thanolamine are used to neutralize the condensate pH. In utility ilers, a *volatile treatment* of hydrazine and ammonia is often plied. The main benefit of hydrazine/ammonia is that it constitutes all-volatile approach by minimizing the introduction of organic nstituents into the system, and provides a lower cost of condensatecontrol. However, an excessive use of ammonia could lead to an vation of condensate pH, with resultant increase in corrosion.

The disadvantage of neutralizing amines for industrial boilers is possible poor control of chemical injection.

Filming amines are used to establish a continuous protective m over the surfaces of after-boiler piping systems. This method prents contact of any potential corrosive steam/condensate contuents with the metal of the piping system. Filming amines are ite often supplemented by the use of neutralizing amines to protect metal from any discontinuity in the protective film. This is espelly applicable to boiler systems operating above 200 psi with 75 rcent or more condensate returns.

Priming, foaming, and carryover. *Priming, foaming,* and *carryover* factors usually controllable by the operating engineer. *Priming* is lifting of boiler water by the steam flow. The water may be lifted as a spr or in a small body; as it enters the steam line, its weig and vel y may cause severe damage to equipment. Ruptu steam-line fittings or wrecked turbines or engines have resulted fr "slugs" of water. Unless priming is induced by faulty boiler des (which is not uncommon), it is caused by carrying too high a wa level for the demands for steam flow. The water level in the dr should be kept several inches lower than normal if the steam fl fluctuates very much, for a sudden rush of steam sometimes tend pick up water from the surface directly below the nozzle.

Operators can avoid priming by:

1. Not forcing or overfiring any boiler connected to steam-usi machinery, such as engines or turbines.
2. Maintaining a constant and steady water level in the boiler an avoiding rapid water level fluctuations.
3. Following good surface and bottom blowdown procedures to elim nate mud and sludge from internal treatment.
4. Avoiding sudden openings of throttle valves to steam-usi machinery.

Scaling of superheater tubes may occur from deposits result from carrying over impurities with water slugs.

Foaming is more a chemical than a mechanical problem. High su face tension of the boiler water causes many of the steam bubbles be encased by a water film. These film-encased bubbles rise and pa out in the steam flow. The cause of high surface tension is usuall high concentration of solids in the boiler water. Organic matter, to may produce this trouble. Periodic checks on boiler-water concent tion and control of blowdown to hold the concentration within allo able limits will prevent foaming. The density of the boiler water is measure of its concentration. Specially calibrated hydrometers a available at low cost for direct reading of this condition, as are co ductivity meters.

The general effect of foaming is a reduction in steam quality increase in the moisture content of the steam. Foaming promo priming and carryover. Foaming may be corrected by (1) using surfa blowdown more frequently until the surface foam has been remove (2) correcting the salt content; remember foaming can be caused by high dissolved salt content in the boiler water as well as excess alkalinity and similar boiler water problems. If the concentrations a found to be high, use the bottom blowdown and feed fresh water dilute the concentration to acceptable levels. Trace the system for a leakage in condensate returns or condensers, and also check the pr

ed dosage of chemical compound treatment to make sure over er-treatment is not occurring.

Antifoaming agents may also suit some plants. As dissolved solids and alkalinity increase in boiler water, foaming and resultant carry- er also increase. Chemical antifoaming agents typically function by coming increasingly insoluble as water temperature increases. omewhere in this higher temperature range, the agents break up e foam, disrupting its cohesive nature and reducing the potential carryover. Silicones, polyglycols, and polyamides are used up to bout 800–900 psi boiler operating pressure. Above this pressure nge, they become undesirable, because their addition increases the spended-solids content of boiler water.

Carryover from steam boilers. Clean steam plays an important part economical power plant operation. When the system is contaminat- with water, mineral solids, or other impurities, numerous troubles velop and costs automatically increase. Foreign matter entrained in herwise clean steam leaving a boiler drum is commonly termed *car- over.* It can be eliminated or minimized by determining its cause d then applying the right correction. The magnitude of the losses casioned by carryover is not generally realized. Fuel consumption, uipment maintenance costs, and plant safety are all affected.

There are many cases where carryover still persists, even though all dinary preventive measures are used. To reduce entrained solids to an solute minimum, steam washers or steam separators are installed. ashers use the relatively pure incoming feedwater to wash outgoing eam. Separators remove entrained water and solids by impinging the eam against baffles or suddenly changing its direction of flow so that reign particles are thrown out by centrifugal force. Separators or puri- ers are also valuable as insurance against any unexpected slugs of ter which might damage power plant equipment.

Total dissolved solids when maintained at too high a concentration the boiler water may cause excessive carryover, which can result in echanical damage and deposits in turbines and feedwater heaters. e measurement of dissolved solids is by conductivity. For most boil- waters 1 micromho = 0.9 ppm dissolved solids. For condensate, the erage is 1 micromho = 0.5 ppm dissolved solids. Dissolved solids ntrol is by blowdown.

Acid attack, or low-pH operation, causes the magnetic iron oxide m on metal surfaces to disappear, and the metal itself is attacked. e loss of metals is in the form of smooth, rolling contours, usually lled *gouging* (see Fig. 13.7*a*). A secondary-type attack could be drogen damage or embrittlement, as hydrogen is released during e acidic attack on the metal, once the oxide coating is lost.

Blowdown. *Blowdown* is an integral part of the proper functionin of a boiler water treatment program and usually requires continuo monitoring for positive control. It is through blowdown that most the dirt, mud, sludge, and other undesirable materials are remove from the boiler drum.

In most systems, surface blowdown is accomplished continuousl and the optimum blowdown interval is such that sludge or scale heating surfaces is minimized. At the same time, the loss of heat a chemical additives is also kept to a minimum.

In the larger, more critical boilers, continuous surface blowdow usually combined with a regular bottom blowdown. In many hig pressure boilers, it is desirable to minimize boiler blowdown to redu heat and water losses.

Blowdown analysis is complicated by sample conditioning conside ations (a sample cooler is usually required), but the control parame is generally conductivity. Typically, a conductivity meter limi maintained within a control range, and blowdown is activated b certain deviation from that range. Other blowdown monitoring pa ameters include pH, silica, hydrazine, and phosphate.

Intermittent or bottom blowdown is taken from the bottom of th mud drum, waterwall headers, or lowest point in the circulation sy tem. The blowoff valve is opened manually to remove accumula sludge, about every 4 to 8 hr, or when the boiler is idle or on a lo steaming rate. But hot water is wasted, and control of concentratio is irregular and requires operator trial-and-error to establish quan ty and time of blowdown.

Continuous *surface* blowdown automatically keeps the boiler wa within desired limits. Continuously removing a small stream of boi water keeps the concentration relatively constant. Savings by transfer heat in the blowdown to incoming makeup often pay for the investmen

Percentage blowdown calculations. There are many operating engine who use cycles of concentration in calculating percentage blowdo The author prefers equating flows as shown in Fig. 13.8 to ob flows of the items listed in the figure. Marine engineers at one used the term "concentration factor." For example, if the feedwa shows 0.5 grains of impurities, and the boiler water shows 15 gra per gallon, the concentration factor is 15/0.5 = 30. From this, the eral equation for percent blowdown was used, namely

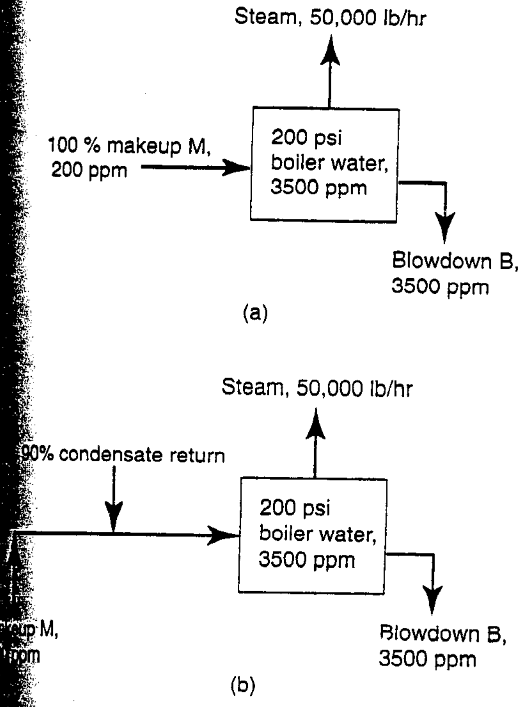
$$\text{Percent blowdown required} = \frac{\text{Feedwater concentration}}{\text{Concentration factor}}$$

Amount of blowdown is calculated as a percentage of makeup flow into the boiler in order to keep the concentration of impuri he boiler at an acceptable level, or at acceptable ppm as shown in ig. 13.3. If no blowdown was performed, the solids concentration in he makeup water would *add* to the existing solids concentration as eam is evaporated. Blowdown removes the concentrated impurities acceptable boiler water concentrations, in modern practice, xpressed in ppm.

The best way to demonstrate the *balance of flow method* in calcu- ting required percentage blowdown is to use an example. See Fig. 13.8*a*.

Example The stated conditions are: A 200-psi boiler generates 50,000 lb/hr steam with 100 percent makeup. An analysis shows boiler water is maintained at 3500 ppm total solids, while makeup is at 200 ppm total solids at 60°F.

1. Find percentage of blowdown required to maintain 3500 ppm total solids in the boiler water.
2. Find blowoff and feedwater flow.
3. See Fig. 13.8*b*. Find blowdown percentage, blowdown, condensate return, and makeup flow for 90 percent condensate return.



13.8 Layout diagram of boiler steam flow, make- nd blowdown assists in calculating percentage own and the flows involved. (*a*) Makeup is 100 (*b*) In this arrangement, makeup is 10 percent.

6

Schroeder, C.D. 1991
Solutions to Boiler and
Cooling Water Problems
New York:
Van Nostrand Reinhold

6 Boiler Tubes

Boiler-Tube Failure

Tube failures in boilers involve either corrosion or mechanical failures, and at times both. Classification is made under what is considered the predominating element in the failure. In considering tube failures, it is important to note the location. For example: is the failure located close to the burners or soot blowers? Is the tube restrained by a boiler drum or tube support?

The largest number of water tube failures occur because of overheating. This accounts for about half of all failures. Fatigue or corrosion fatigue account for approximately one-quarter of the failures. Stress corrosion, pitting, corrosion, *hydrogen embrittlement*, etc. account for the remaining failures.

Steel tube and boilers generally depend on a *magnetite* (Fe_3O_4) film for protection from chemcial attack. Breakdown of this film is often involved in tube failures. Magnetite is soluble at a pH below 5.0 or above 13.0. Minimum corrosion takes place at a pH range of 9.0–11.0.

used ectly, corrosion of boiler systems can result from oxygen and/or the decomposition of sodium sulfite.

The usual sodium sulfite residual in boiler water is 20–40 ppm. Sulfite should be added as far back in the system as possible; in most systems, this is the storage area of the deaerator. The fastest sulfite-oxygen reaction occurs at a pH of 9.0–10.0. Below and above these values, the reaction rates decrease. The reaction is also very slow at temperatures below 200°F.

If sulfite is added to the boiler drum, oxygen may react with the metal surface before it reacts with the sulfite. Sodium sulfite normally contains a catalyst to speed the oxygen-sulfite reaction; cobalt sulfate or chloride are most commonly used.

Where possible, the sulfite should be added alone to the deaerator storage. Many antifoam compounds, chelants, and polymers react with the cobalt catalyst, rendering it ineffective. Many water treatment problems involve a trade-off. Polymers and sodium sulfite are both more effective if added to the deaerator storage rather than to the boiler drum. The proper solution might be to evaluate the importance of the problem. If a corrosion problem exists, add the sodium sulfite alone to the deaerator and the polymer sludge conditioner to the boiler drum or feed line. On the other hand, if the main problem involves scale control, add the polymer to the deaerator storage area with the sodium sulfite.

At high boiler pressures, sodium sulfite decomposes; the usual decomposition boiler pressure limitation recommended is 900 psig. Under high-temperature/pressure conditions, generation of sulfides and sulfur dioxide can result in corrosion in both the condensate and boiler systems.

Also, there is evidence that decomposition takes place in the high-heat-transfer area of medium-pressure boilers. This can result in possible scale and corrosion in the boiler tubes. Since decomposition takes place only at the metal/scale interface, the condensate system is not affected.

Decomposition of sulfites in medium-pressure boilers most often involves oil-fired boilers; in the furnace area, oil-fired boilers release a much larger amount of radiant heat than gas-fired units. The solution to this problem is to change from sodium sulfite to hydrazine.

Sodium sulfite should not be relied on to protect a boiler from corrosion when the boiler is off-line for a weekend or overnight. The correct procedure is to maintain low steam pressure in the boiler or a *nitrogen blanket*. This prevents inleakage of air.

When sodium sulfite is dissolved in a mix tank, only enough agitation should be used to dissolve the chemical completely. If agitation is continued, sulfite will react with air in the atmosphere.

When a sudden increase in sulfite dosage occurs, an investigation should be made to determine the source of increased oxygen in the system. Quite often, a malfunction of the deaerator is responsible. This is discussed in Chapter 4.

Caustic Soda. Where corrosion is concerned, caustic soda has some properties similar to sodium sulfite. Both chemicals assist in preventing corrosion in low- and medium-pressure boilers; both chemicals can cause corrosion in high-pressure systems.

Caustic soda is added as an integral part of a water treatment program. It can also be formed in a boiler as a result of the decomposition of bicarbonates or carbonates present in makeup water. As stated, caustic soda alkalinity (OH) in boiler water normally aids in the prevention of corrosion. Refer to Table 5-1, Guidelines for Water Quality in Industrial Water Treatment Boilers, for recommended caustic alkalinity. When caustic alkalinity is high, it can be reduced by increased blowdown. If low, it can be increased by the addition of caustic soda. Even at very high caustic alkalinities, few corrosion problems can be traced to the presence of caustic soda in low- and medium-pressure boilers.

In the period during which boiler drums were riveted, caustic soda concentrated under the rivets and caused *caustic cracking* (Fig. 6-2). This problem has virtually disappeared since very few riveted boilers are still in operation. Caustic cracking forms black magnetic iron oxide, Fe_3O_4. Oxygen is also involved in the pitting attack, which often occurs during acid cleaning.

There are several reasons why oxygen is usually not involved in the corrosion of operating boilers. First, deaerators remove most of the oxygen in the preboiler cycle. When oxygen does enter a boiler drum, the boiler itself acts as a deaerator, and oxygen leaves the boiler with the steam. Finally, very few boilers operate without oxygen scavengers, such as sodium sulfite or hydrazine.

Nevertheless, boiler tubes or drums pitted from oxygen attack are not uncommon. As a solution, the first step should be to investigate the operating cycle of the boiler. It should be determined if the boiler is off the line during some portion of the day or on weekends. The resulting condensation of steam in the boiler drum creates a vacuum and draws in air; oxygen pitting can follow. Even maintaining a high residual of sodium sulfite will not prevent this type of attack. The most effective solution is to maintain a small amount of steam pressure or a nitrogen blanket during the period the boiler is off-line.

To repeat, only a small number of oxygen corrosion cases take place when a boiler is operating. To maintain this condition, the oxygen level in the feedwater should be kept at a low level. Field oxygen analyzers are now available through a number of industrial water treatment companies. The feedwater oxygen level should be checked at least once every year.

When the oxygen level is high (>8 ppb), an investigation should be made of the deaerator operation. In-leakage of oxygen at the feed pump is also possible. Refer to Chapter 4, Faulty Deaerator Performance.

Oxygen can also contribute to pitting corrosion during acid cleaning. High temperatures will aggravate the attack. Oxygen attack will also be increased if the acid corrosion inhibitor is adsorbed on scale present in the boiler. Under such conditions, the inhibitor will not be available to protect the metal.

To prevent oxygen corrosion in operating boilers, the oxygen scavengers should be added as far back as possible in the preboiler system. Usually, the location will be the deaerator storage area.

Sodium sulfite is usually catalyzed to speed the reaction with oxygen. To protect the catalyst, the sodium sulfite should not be mixed with other water treatment chemicals.

Bicarbonates and Carbonates. Alkalinity in raw water is normally in the bicarbonate form. When the water is heated in a deaerator, the bicarbonate is converted to carbonate plus some caustic soda. Depending on boiler pressure, this reaction is carried further to completion in the boiler.

All the remarks pertaining to caustic soda that appeared earlier in this chapter under Caustic Soda also apply to bicarbonates and carbonates that are present in feedwater.

There is also a corrodant that develops in the decomposition of carbonates to caustic soda. Carbon dioxide is formed. This gas will be carried out of the boiler with steam to form carbonic acid in the condensate. The solution is to treat the condensate to neutralize the carbonic acid.

Chlorides. Oxygen pits in boilers are aggravated by chloride ions. Chlorides are removed in demineralized makeup water for high-pressure boilers, but chlorides can still enter a high-pressure boiler system through leaks. For middle- or low-pressure boilers, no effort is made to remove the chlorides present in the feedwater. In fact, if a sodium cation ion exchanger is employed, the chloride level often increases through poor rinsing of the resin.

Every effort should be made to rinse the ion-exchange bed efficiently. When a demineralizer is used, the efficient use of this equipment will remove all chlorides.

The chloride content is especially important when a boiler is used in cycling operation; that is, the boiler may be shut down in the evenings or on weekends. Should oxygen enter the boiler, the chlorides present will aggravate the corrosion process.

er, a boiler feedwater heater is merely one use of a shell and tube exchanger. They are also employed in industry to heat and cool many different products. Where steam is used on the shell side, the problems encountered are similar, regardless of the liquid on the tube side. One major exception is leakage, where a product can contaminate the steam or the steam can enter the product side.

Although different problems exist on the shell (steam) and tube (feedwater) sides, they are interrelated. Any change in performance on one side affects the other. Usually, if the temperature and flow rate of the feedwater and the pressure of the inlet steam are the same as designed, then all other operating factors should remain constant. Any changes in pressure and temperature can indicate a possible problem.

The quality and operating conditions of the steam have a definite effect on the heat transfer as well as the life of the equipment. The operating engineer has no control over design of the heat-transfer equipment but, in many cases, he can modify the quality of the steam and the methods of operation.

When a feedwater heater fails to deliver the required feedwater temperature, a check of the steam pressure on the shell side should be made. Also, any accumulation of water in the shell should be noted. If these checks prove satisfactory, other factors should be investigated.

Corrosion

pH. The pH of the condensing steam should be in the general range of 8.3–8.5. A pH of 6.0 or lower can result in the corrosion of most materials of construction used in heat exchangers. Neutralizing amines are commonly used to control the pH; in some cases, no pH adjustment is made, but filming amines are used to form a protective film throughout the steam condensate system. Deaerator performance should be reviewed to make certain that all free carbon dioxide is being removed.

High-pressure boilers use demineralized feedwater, which contains virtually no carbonate, but carbonate is present in low-and medium-pressure units. Breakdown of carbonate alkalinity is responsible for the formation of carbon dioxide and low-condensate pH. If alkalinity addition is required in boiler water, caustic soda can be used instead of soda ash. Caustic soda does not form carbon dioxide as a decomposition product. Various types of pretreatment can also be used to reduce carbonate alkalinity. (Refer to the material on carbon dioxide in Chapter 8.)

Ammonia. Ammonia will corrode copper-bearing alloys, resulting in stress corrosion cracking or grooving. Attack is aggravated by the presence of oxygen. Dosages of nitrogen containing water treatment chemicals such as neutralizing amines, filming amines, and hydrazine should be held to a minimum. Another source of ammonia is polluted makeup water.

Mechanically, performance of the deaerator should be checked so that ammonia is held to a minimum. Chemically, high-pH makeup water in a deaerator will result in more ammonia release than a unit operating at a medium-pH range such as 7.0–8.0.

Oxygen and Carbon Dioxide. These two gases are present in most steam systems to some degree. Both gases intensify ammonia attack on copper alloys. Oxygen alone is the principal cause of pitting of steel, while carbon dioxide causes grooving.

Oxygen is usually held to a minimum by deaeration and the use of oxygen scavengers; only free carbon dioxide is removed in the deaerator. Various dealkalizing pretreatment methods assist in removing combined carbon dioxide such as bicarbonates and carbonates. Air leakage into any part of the steam condensate system will contribute to oxygen and carbon dioxide; the only solution is locating and repairing the leaks. During shutdown periods, *nitrogen blankets* can be used to prevent air in-leakage.

Deaerator performance should also be checked; ammonia removal will be more effective at high pH levels than at neutral or low levels.

Types of Corrosion Encountered

Designs, temperatures, and materials of construction of feedwater heaters vary. Accordingly, many types of corrosion are encountered. These include (1) general, (2) pitting, (3) stress, corrosion cracking, (4) impingement, (5) cavitation, and (6) crevice.

Since these classifications of corrosion are covered under cooling water corrosion problems, they are not repeated here. The reader is referred to Chapter 9.

Deposits

In high-pressure boiler systems, deposits are seldom a problem in feedwater heaters. Makeup is demineralized water, and condensate polishers remove any returning contaminants.

Where lower-pressure boilers are concerned, deposits usually result from faulty pretreatment or in-leakage. In such cases, the solution lies in correcting the faulty pretreatment or in taking steps to stop the leakage.

Economizer Corrosion and Deposits

Corrosion

Corrosion is the primary problem encountered with economizers on both the water and gas sides. Most corrosion occurs on the gas side through condensation of sulfuric acid but, as the title of this book suggests, only water side corrosion will be covered here.

The primary water side corrodent is oxygen, which can cause severe pitting. Unlike a boiler, where oxygen can be released in the steam drum, the oxygen in an economizer is trapped. Since no water treatment steps can be taken in an economizer, the answer to the problem is to remove all oxygen before the boiler feedwater enters the economizer. This means operating the deaerator efficiently and adding a sufficient amount of sodium sulfite or hydrazine to the deaerator storage. It is also possible that leakage of oxygen into the boiler feed pumps can take place.

Most economizers are of the horizontal type. Water can enter from the top or bottom. Water entering from the top is much more liable to trap air and initiate corrosion. It is also important in economizer corrosion control to maintain a pH of 8–9. At times, this is accomplished by recycling a small amount of boiler water. Most economizers are not of the steaming type. This is especially true of high-makeup boiler plants. As a general rule, the economizer water should be 40–50°F below the temperature of steam formation (Shields, 1961, pp. 274–282). Failure to keep economizer water within this temperature range can result in *water hammer*, with possible equipment damage.

Of probably greater importance in the corrosion of economizers is shutdown time. As with boilers, dry storage is preferred for long idle periods, while wet storage is preferred for short periods. For dry storage, all water should be drained or blown from the tubes. Heat should be applied to make certain all moisture is removed. Finally, the unit should be sealed and protected with a nitrogen blanket. For wet storage, deaerated water should be used: to this, about 100 ppm of hydrazine should be added.

High water temperatures (250°F) are advantageous for the economizer since they assist in preventing the condensation of sulfuric acid on the gas side. If possible, the pressure of the deaerator can be raised, or a heat exchanger can be used before the economizer. Adversely, if the temperatures are too high, steam may form. Water hammer can follow. Oxygen pitting is the major type of economizer corrosion. But where deposits form, it is also possible for caustic to concentrate underneath the deposits. Caustic gouging can result.

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CARCINOGENICITY/TOXICOLOGY STUDIES (COLUMN 3):
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MR = MALE RATS; FR = FEMALE RATS; MM = MALE MICE; FM = FEMALE MICE
14-SD (ACUTE), 14-RD (REPEAT DOSE), 90-DAY (SUBCHRONIC), AND CHRONIC

ROUTE CODES

FEED	DOSED-FEED	GAV	GAVAGE	IM	INTRAMUSCULAR INJECTION
INHAL	INHALATION	IP/IJ	INTRAPERITONEAL INJECTION	IT	INTRATRACHEAL
IVAG	INTRAVAGINAL	MICRO	MICROENCAPSULATION IN FEED	SC&GV	SUBCUTANEOUS INJ. + GAVAGE
SC/IJ	SUBCUTANEOUS INJECTION	SP	TOPICAL	WATER	DOSED-WATER

For each separate carcinogenicity experiment (male rats, female rats, male mice, female mice), one of the following codes is selected to describe the findings. The categories refer to the strength of the experimental evidence and not to either potency or mechanism.

CE Clear Evidence of Carcinogenic Activity is demonstrated by studies that are interpreted as showing a dose-related (i) increase of malignant neoplasms, (ii) increase of a combination of malignant and benign neoplasms, or (iii) marked increase of benign neoplasms if there is an indication from this or other studies of the ability of such tumors to progress to malignancy.

SE Some Evidence of Carcinogenic Activity is demonstrated by studies that are interpreted as showing a chemically-related increased incidence of neoplasms (malignant, benign, or combined) in which the strength of the response is less than that required for clear evidence.

EE Equivocal Evidence of Carcinogenic Activity is demonstrated by studies that are interpreted as showing a marginal increase of neoplasms that may be chemically related.

NE No Evidence of Carcinogenic Activity is demonstrated by studies that are interpreted as showing no chemically-related increases in malignant or benign neoplasms.

IS Inadequate Study of Carcinogenic Activity is demonstrated by studies that because of major qualitative or quantitative limitations cannot be interpreted as valid for showing either the presence or absence of carcinogenic activity.

Earlier designations include:

P Positive	E Equivocal	N Negative

ABBREVIATIONS USED IN THIS REPORT AND INFORMATION CONTACTS:

CHEMICAL DISPOSITION/SPECIAL STUDIES (COLUMN 4): FOR ADDITIONAL INFORMATION, CONTACT THE CENTRAL DATA MANAGEMENT GROUP AT 919-541-3419.

CHEMICAL DISPOSITION/SPECIAL STUDIES TESTTYPES AND CODES:

BIOSAMPLE METHOD DEVELOPMENT (BSMD)
CHEMICAL DISPOSITION (CHEM DISP)
CELL PROLIFERATION (CELL PROLIF)
HUMAN METABOLISM (HUMAN METAB)

METABOLISM
MECHANISMS
ROUTINE BIOSAMPLE ANALYSIS (RBSA)
TOXICOKINETIC STUDY (TKS)

GENETIC TOXICOLOGY (COLUMN 5): FOR ADDITIONAL INFORMATION, CONTACT THE CENTRAL DATA MANAGEMENT GROUP AT 919-541-3419.

GENETIC TOXICOLOGY TESTTYPE CODES:

SA, SA-N	- SALMONELLA
SR	- SALMONELLA REDUCTION
ML, ML-N	- MOUSE LYMPHOMA
DL	- DROSOPHILA (SLRL/RT)
CY	- IN VITRO CYTOGENETICS (CA/SCE)
SH	- SHE CELL TRANSFORMATION

IN VIVO CYTOGENETICS:

MN	- MICRONUCLEUS
CA	- CHROMOSOME ABERRATIONS
SC	- SISTER CHROMATID EXCHANGES

RESULTS CODES

+	- POSITIVE RESPONSE
+W	- WEAKLY POSITIVE
-	- NEGATIVE RESPONSE
?	- INCONCLUSIVE

-/-	- (DL) SEX-LINKED RECESSIVE LETHAL/RECIPROCAL TRANSLOCATION
-/-	- (CY) CHROMOSOME ABERRATIONS/SCE'S
-/-	- (MN) MALE/FEMALE

ORGAN SYSTEMS TOXICITY (COLUMN 6): FOR ADDITIONAL INFORMATION, CONTACT THE CENTRAL DATA MANAGEMENT GROUP AT 919-541-3419.

SYSTEMS TOXICITY TESTTYPE CODES:

*	BSLT	- BIOCHEMICAL SPECIFIC LOCUS TEST
*	DLF/DLM	- DOMINANT LETHAL FEMALE/MALE
	IMM	- IMMUNOTOXICITY, SENSITIZER, ASTHMOGENIC
*	MSLT	- MORPHOLOGICAL SPECIFIC LOCUS TEST
*	PZE	- PREIMPLANTATION ZYGOTE EFFECTS
	RDGT	- REPRO/DEV GEN TOX (28-DAY)
	STIV	- SHORT-TERM IN VIVO REPRO. TOX.
	TRC	- TOTAL REPRODUCTIVE CAPACITY

	DLA	- DOMINANT LETHAL
*	HTT	- HERITABLE TRANSLOCATION TEST
	JPA	- JUVENILE PESTICIDE ASSESSMENT
	NTA	- NEUROTOXICOLOGY ASSESSMENT
	RACB	- CONTINUOUS BREEDING
	SPINH	- SPERMIATION INHIBITION
	TER	- CONVENTIONAL TERATOLOGY
	TRP	- TERATOLOGY PILOT STUDIES

Immunotox: For the purposes of these studies, positives (+) were established on the basis that the test material produced a significant dose-response effect, excluding body weight, in any one or more tests or significantly ($P<0.05$ vs. control values) altered two or more tests at the highest dose level tested.

Sensitizer: Positives (+) indicate contact sensitizer positive in guinea pigs and/or mouse.

Publication numbers identified as "PUB #" in this column refer to the publication list on the following page.

* Testtype codes for Germ Cell Publication/Studies

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T. K. Thomas and E. M. Sfakiotakis, "Effect of Low-Oxygen Atmosphere on Storage Behaviour of Kiwifruit," *Advances in Horticultural Science* **11**, 137–141 (1997).

A. B. Truter, J. C. Combrink, and S. A. Burger, "Control of Superficial Scald in Granny Smith Apples by Ultra-Low Levels of Oxygen as an Alternative to Diphenylamine," *Journal of Horticultural Science* **69**, 581–587 (1994).

R. K. Voltz et al., "Prediction of Controlled Atmosphere-Induced Flesh Browning in Fuji Fruit," *Postharvest Biology and Technology* **13**, 97–102 (1998).

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H. S. Yong, I. I. Kim, and L. C. Jae, "Effects of Harvest Maturity and Storage Environments on the Incidence of Watercore, Flesh Browning, and Quality in Fuji Apples," *Journal of the Korean Society for Horticultural Sciences* **39**, 569–573 (1998).

P. Younmoon et al., "Preharvest Factors Affecting the Incidence of Physiological Disorders During CA Storage of Fuji Apples," *Journal of the Korean Society for Horticultural Sciences* **38**, 725–729 (1997).

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See also PACKAGING: PART IV—CONTROLLED/MODIFIED ATMOSPHERE/VACUUM FOOD PACKAGING.

CORN. See CEREALS SCIENCE AND TECHNOLOGY.

CORROSION AND FOOD PROCESSING

MATERIALS OF CONSTRUCTION

The "Stainless Steels"

Many people refer to this range of alloys as austenitic stainless steels, 18/8s, 18/10s, etc, without a full appreciation of what is meant by the terminology. It is worth devoting a few paragraphs to explain the basic metallurgy of stainless steels.

It was in 1913 that Harry Brearley discovered that the addition of 11% chromium to carbon steel would impart a good level of corrosion and oxidation resistance, and by 1914 these corrosion resisting steels had become commercially available. It was Brearley who pioneered the first commercial use of these steels for cutlery, and it was also he who coined the name "stainless steels." For metallurgical reasons, which are outside the scope of this article, these were known as ferritic steels because of their crystallographic structure. Unfortunately, they lacked the ductility to undergo extensive fabrication and furthermore, they could not be welded. Numerous workers tried to overcome these deficiencies by the addition of other alloying elements and to produce a material where the ferrite was transformed to austenite (another metallurgical phase) that was stable at room temperature. Soft stainless steels that were ductile both before and after welding were developed in Sheffield, England (then the heart of the British steel industry) exploiting scientific work undertaken in Germany. This new group of steels was based on an 18% chromium steel to which nickel was added as a second alloying element. These were termed the austenitic stainless steels. The general relationship between chromium and nickel necessary to maintain a fully austenitic structure is shown diagrammatically in Figure 1. It will be seen that the optimum combination is 18% chromium, 8% nickel—hence the terminology 18/8s.

Probably the next major advance in the development of stainless steels was the discovery that relatively small additions of molybdenum had a pronounced effect on the corrosion resistance, greatly enhancing the ability to withstand the effects of mineral acids and other corrodents such as chloride solutions. Needless to say, from these early developments, there has been tremendous growth in production facilities and the number of grades of stainless steel available. Table 1 lists some of the more commonly available grades, while Figure 2 illustrates how the basic 18/8 composition is modified to enhance specific physical or chemical properties.

In spite of the plethora of stainless steels available, grades 304 and 316 have, and continue to be, the workhorses for fabrication of dairy and food processing equipment.

Although 316 stainless steel offers excellent resistance to a wide range of chemical and nonchemical environments, it does not offer immunity to all. In the case of the food industry, these are notably anything containing salt, especially low-pH products. There was, therefore, a demand by industry to develop more corrosion-resistant materials and these are finding increasing use in the food industry for certain specific processing operations.

Super Stainless Steels and Nickel Alloys

The super stainless steels are a group of alloys that have enhanced levels of chromium, nickel, and molybdenum compared to the conventional 18/8s. The major constituent is still iron; hence the classification under the "steel" title

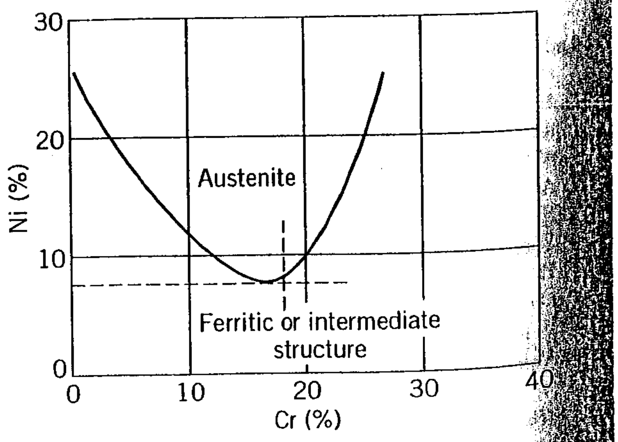

Figure 1. Graph showing the various combinations of chromium and nickel that form austenitic stainless steels. *Source:* Ref

Table 1. Composition of Some of the More Commonly Used Austenitic Stainless Steels

Alloy	UNS no.	Composition (%) Carbon	Manganese	Silicon	Chromium	Nickel	Molybdenum	Others
302	S30200	0.15	2.00	1.00	16.0–18.0	6.0–8.0		Sulfur 0.030
304	S30400	0.08	2.00	1.00	18.0–20.0	8.0–10.5		Phosphorus 0.045 Sulfur 0.030
304L	S30403	0.03	2.00	1.00	18.0–20.0	8.0–12.0		Phosphorus 0.045 Sulfur 0.030
316	S31600	0.08	2.00	1.00	16.0–18.0	10.0–14.0	2.0–3.0	Phosphorus 0.045 Sulfur 0.030
316L	S31603	0.03	2.00	1.00	16.0–18.0	10.0–14.0	2.0–3.0	Phosphorus 0.045 Sulfur 0.030
317	S31700	0.08	2.00	1.00	18.0–20.0	11.0–15.0	3.0–4.0	Phosphorus 0.045 Sulfur 0.030
317L	S31703	0.03	2.00	1.00	18.0–20.0	11.0–15.0	3.0–4.0	Phosphorus 0.045 Sulfur 0.030
321	S32100	0.08	2.00	1.00	17.0–19.0	9.0–12.0		Phosphorus 0.045 Sulfur 0.030
347	S34700	0.08	2.00	1.00	17.0–19.0	9.0–13.0		Ti ≮ 5 × Carbon Sulfur 0.030 Cb + Ta ≮ 10 × Carbon

Note: Unless indicated otherwise, all values are maxima.

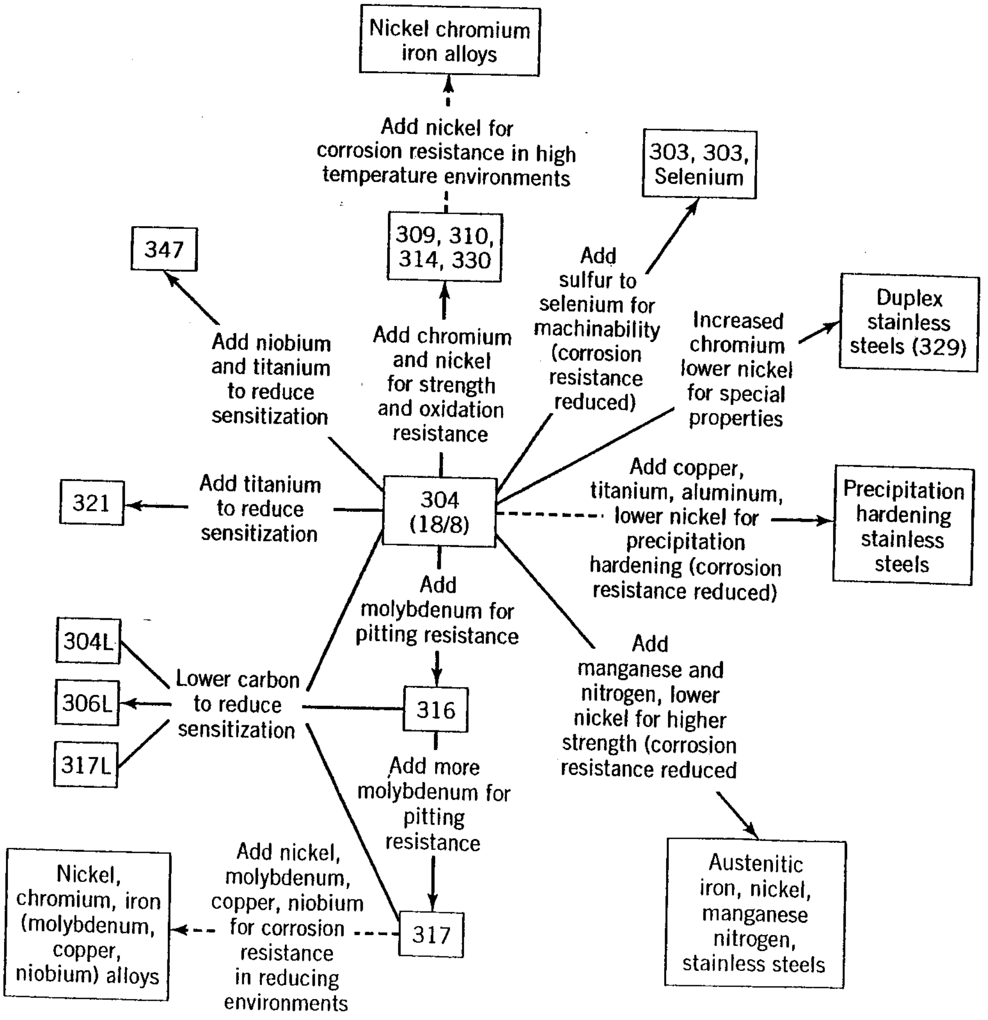

Figure 2. Outline of some compositional modifications of 18/8 austenitic stainless steel to produce special properties. *Source:* Ref. 2.

Still further increases in the three aforementioned alloying elements result in the nickel alloys. (The classification of an alloy is generally under the heading of the major constituent.)

There are a large number of these alloys but those of primary interest to the food industry are shown in Table 2 together with their composition. In general terms, it will be noted that the increase in nickel content is accompanied by an increase in chromium and molybdenum. As stated previously, this element is particularly effective in promoting corrosion resistance.

Just like insurance, you get only what you pay for, and generally speaking, the higher the corrosion resistance, the more expensive the material. In fact, the differential between type 304 stainless steel and a high-nickel alloy may be as much as 20 times, depending on the market prices for the various alloying elements that fluctuate widely with the supply and demand position.

Aluminum

High-purity grades of aluminum (±99.5%) and its alloys still are preferred for some food and pharmaceutical applications because of the reasonable corrosion resistance of the metal. This resistance is attributable to the easy and rapid formation of a thin, continuous, adherent oxide film on exposed surfaces. This oxide film, in turn, exhibits a good corrosion resistance to many foodstuffs, and it is reported that fats, oils, sugar, and some colloids have an inhibitory or sealing effect on these films (3).

As aluminum salts formed by corrosion are colorless, tasteless, and claimed to be nontoxic, the metal is easy to clean, inexpensive, and light and has a high thermal conductivity. It still is used quite extensively in certain areas of food manufacture and distribution. However, in recent years, the claim of nontoxicity is being questioned as a high dietary incidence has been implicated in Alzheimer's disease (senile dementia) with compounds of aluminum (aluminosilicates) being found in the brain tissue of sufferers (4). However, the case is far from proven, and it is not clear if the increased levels of aluminosilicates are due to a high intake of aluminum per se or other factors such as a dietary deficiency of calcium.

For many years, aluminum was used extensively for containment vessels in the diary and brewing industry, and it was Richard Seligman who founded the then Aluminium Plant and Vessel Company (now APV plc) to exploit the technique of welding this material for the fabrication of fermenting vessels in the brewing industry (5). Many of these original vessels are still in use in some of the smaller, privately owned breweries in the United Kingdom.

Although large fermenting vessels and storage tanks now tend to be fabricated from stainless steels, there is still widespread use of aluminum for beer kegs, beer cans, and a miscellany of small-scale equipment where the resistance of aluminum is such that it imparts no change or modification of flavor, even after prolonged storage.

While still used for holding vessels and some equipment when processing cider, wines, and perry, prolonged contact is inadvisable because of the acidity of the sulfites employed as preservatives for these products—inadvisable, that is, unless the surface of the metal has been modified by anodizing or has been protected with a lacquer.

In the manufacture of preserves, aluminum is still employed for boiling pans, the presence of sugar appearing to inhibit any corrosion. In the field of apiculture, it has even been used for making prefabricated honeycombs, which the bees readily accepted.

Extensive use is made of aluminum and the alloys in the baking industry for baking tins, kneading troughs, handling equipment, etc.

In other areas of food manufacture and preparation, the use of aluminum extends virtually over the whole field of activity—butter, margarine, table oils, and edible fats, meat and meat products, fish and shellfish, certain sorts of vinegar, mustards, spices; the list is almost endless.

No mention has so far been made of the application of this metal in the dairy industry, and indeed it still has limited application mostly in the field of packaging, eg, bottle caps, wrapping for cheese, butter, carton caps for yogurt, cream.

It will be appreciated that the uses of aluminum in the food industry so far mentioned have tended to be for equipment used in batch operation, hand utensils, and packaging. There are probably three major factors that have mitigated against its more widespread use, not only in the dairy industry but in brewing and many other branches of food processing.

1. Modern, highly automated plants operating on a continuous or semicontinuous basis employ a wide va

Table 2. Composition of Some of the More Commonly Used Wrought Super Stainless Steels and Nickel Alloys

		Composition (%)						
Alloy	UNS no.	Carbon	Silicon	Manganese	Chromium	Nickel	Molybdenum	Others
904L	N08904	0.02	0.70	2.0	19.0–21.0	24.0–26.0	4.2–4.7	Cu 1.2–1.7
Avesta 254 SMO	S31254	0.02	0.80	2.0	19.5–20.5	17.5–18.5	6.0–6.5	Cu 0.5–1.0, N 0.18–0.22
Incoloy 825	N08825	0.05	0.50	1.0	19.5–23.5	38.0–46.0	2.5–3.5	Al 0.2, Ti 0.6–1.2
Hastelloy G-30	N06030	0.03	0.08	1.5	28.0–31.5	Bal.	4.0–6.0	Co 5.0, Cu 1.0–2.4, Cb + Ta 0.3 Fe 13.0–17.0
Inconel 625	N06625	0.10	0.50	0.50	23.0–28.0	Bal.	8.0–10.0	Co 1.0, Fe 5.0, Al 0.4, Ti 0.4
Hastelloy C-276	N10276	0.02	0.08	1.0	14.5–16.5		15.0–17.0	W 3.0–4.5, V 0.35

Note: Unless indicated otherwise, all values are maxima.

riety of materials of construction. Because of the position in the electrochemical series (to be discussed later), aluminum and its alloys are susceptible to galvanic corrosion when coupled with other metals.

2. The commercial availability of stainless steels and their ease of fabrication, strength, ease of maintenance, appearance, and proven track record of reliability.
3. The fact that since modern plants operate on a semicontinuous basis with much higher levels of fouling, cleaning regimes require strongly alkaline detergents to which aluminum has virtually zero corrosion resistance.

Copper and Tinned Copper

Copper and tinned copper were used extensively in former times because of their excellent thermal conductivity (8 times that of stainless steel), ductility, ease of fabrication, and reasonable level of corrosion resistance. However, the demise of copper as a material of construction is largely attributable to the toxic nature of the metal and its catalytic activity in the development of oxidative rancidity in fats and oils. Even at the sub-part-per-million level, copper in vegetable oils and animal fats rapidly causes the development of off-flavors. In equipment where high levels of liquid turbulence are encountered (eg, plate heat exchanger or high-velocity pipe lines) copper is subject to erosion. Nevertheless, there is an area of the beverage industry where copper is still the only acceptable material of construction, ie, pot stills for Scotch and Irish whiskey production. It is also used in the distillation of the spirits such as rum and brandy. Much old copper brewing equipment such as fermenting vessels and wort boilers is still in use throughout the world, and an interesting observation is that even though the wort boilers in modern breweries are fabricated from stainless steel, they are still known as "coppers" and UK craftsmen fabricating stainless steel are still known as coppersmiths.

Titanium

There are certain areas of the food industry, especially in equipment involving heat transfer, where stainless steels are just not capable of withstanding the corrosive effects of salty, low-pH environments. Food processors are increasingly accepting the use of titanium as an alternative, in the full knowledge that it offers corrosion immunity to the more aggressive foodstuffs and provides a long-term solution to what was an on-going problem with stainless steels. Titanium is a light metal, the density of which is almost half that of stainless steels. Although relatively expensive (6–7 times the cost of stainless steel), being a low-density material offsets this price differential for the raw material by almost half. It is ductile and fabricable using normal techniques, although welding it does require a high degree of expertise.

Other Metals

Tin, in the form of tin plate, is used extensively in the canning industry, where its long-term corrosion resistance to a wide range of food acids makes it a material par excellence for this purpose.

Cadmium, used as a protective coating for carbon steel nuts and bolts, was favored at one time. However, the high toxicity of the cadmium compounds has come under increasing scrutiny from many health regulatory bodies and now cadmium-plated bolting is not permitted in food factories. Indeed, Denmark and Sweden have totally banned the import of cadmium-plated components into their countries, and many other countries are likely to follow suit.

Lead and lead-containing products are generally not acceptable for food contact surfaces, although some codes of practice permit the use of lead-containing solder for capillary pipeline joints on water supplies and service lines.

SELECTING MATERIALS OF CONSTRUCTION

Designing equipment is a multidiscipline exercise involving mechanical engineers, materials–corrosion engineers, stressing experts, draftsmen, etc. The corrosion engineer has an important role in this team effort, namely, to ensure the materials specified will offer a corrosion resistance that is just adequate for all the environmental conditions likely to be encountered during normal operation of the equipment. A piece of equipment that prematurely fails by corrosion is as badly designed as one in which the materials have been overspecified. Unfortunately, all too often the functional requirements for a piece of equipment are analyzed in a somewhat arbitrary manner and all too often, the basic cost of the material tends to outweigh other equally important considerations (6).

Figure 3 shows the primary criteria that must be considered in the initial selection process.

- *Corrosion Resistance.* For any processing operation, there will be a range of materials that will offer a corrosion resistance that is adequate (or more than adequate) for a particular job. When considering corrosion resistance, the operational environment is the obvious one, but the other point must be whether the material will also offer corrosion resistance to the chemicals used for cleaning and sanitizing.
- *Cost.* Many of the materials originally considered will be eliminated on the grounds of their high cost. For example, there is no point in considering a high-nickel alloy when a standard 300 series stainless steel at a lower cost will be perfectly satisfactory.

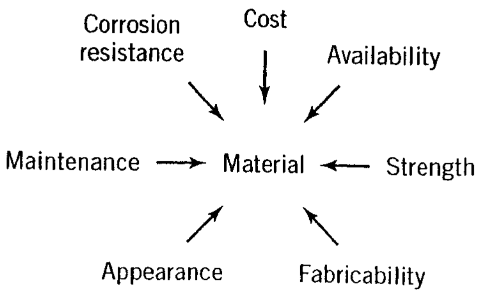

Figure 3. Materials selection criteria.

- *Availability.* Availability is a less obvious feature of the material selection process. Many steel producers will require a minimum order of, say, 3 tons for a nonstandard material. Clearly, the equipment manufacturer is not going to buy this large quantity when the job that is to be done may only require the use of one ton of material.
- *Strength.* Strength is a factor that is taken into account at the design stage but, as with all the others, cannot be considered in isolation. For example, many of the new stronger stainless steels, although more expensive on a ton-for-ton basis than conventional stainless steels, are less expensive when considered on a strength/cost ratio.
- *Fabricability.* There is little point in considering materials that are either unweldable (or unfabricable) or can be welded only under conditions more akin to a surgical operating theater than a general engineering fabrication shop.
- *Appearance.* Appearance may or may not be an important requirement. Equipment located outside must be resistant to environmental weathering and therefore may require the application of protective sheathing, which could double the basic material cost.
- *Maintenance.* Is the equipment to be essentially maintenance-free or is some maintenance, such as periodic repainting, tolerable? How long will the equipment operate without the need for major servicing?

When all these interrelated criteria have been considered, the long list of possible starters will have been reduced to maybe one or two. Also, somewhere through the selection process some of those materials initially rejected because, for example, of their high cost, may have to be reconsidered because of other factors.

TYPES OF CORROSION

Defining Corrosion

Before embarking on a discussion of the various forms of corrosion, it is worthwhile considering exactly what corrosion is. There are several definitions of corrosion. For example, Fontant (7) defines it as extractive metallurgy in reverse using the diagram, shown in Figure 4, to illustrate the point.

A more general and descriptive definition is "it is the deterioration or destruction of a material through interaction with its environment." This covers all materials of construction including rubber and plastics as well as metal. However, the primary object of this article is to deal with corrosion of metals, in particular stainless steels, and how this corrosion can be classified.

There are two basic forms of corrosion—wet corrosion and dry corrosion. Dry corrosion is concerned with the oxidation of metals at high temperature and clearly outside the scope of this text. Wet corrosion occurs in aqueous solutions or in the presence of electrolytes and is an electrochemical process. It should be noted that the "aqueous" component of the system may be present in only trace quantities (eg, present as moisture); the classical example is the corrosion of steel by chlorine gas. In fact, steel is not corroded by chlorine since steel is the material used for storing liquid chlorine. However, in the presence of even trace quantities of moisture, chlorine rapidly attacks steel and, for that matter, most metals.

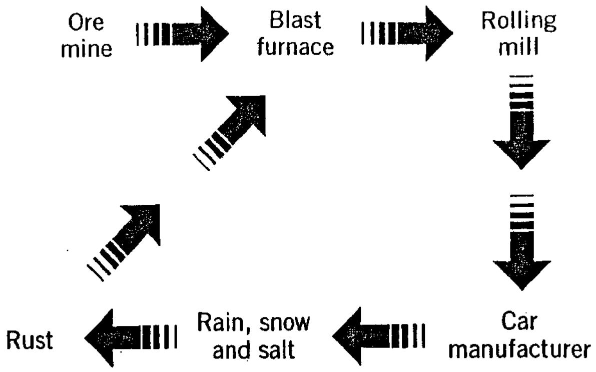

Figure 4. Extractive metallurgy in reverse.

The corrosion of metals involves a whole range of factors. These may be chemical, electrochemical, biological, metallurgical, or mechanical, acting singly or conjointly. Nevertheless, the main parameter governing corrosion of metals is related to electrochemistry. Electrochemical principles therefore are the basis for a theoretical understanding of the subject. In fact, electrochemical techniques are now the standard method for investigating corrosion although the standard "weight loss" approach still provides invaluable data. It is not proposed to discuss in depth the electrochemical nature of corrosion but should further information be required, several excellent texts are available (7,8).

Forms of Corrosion

Wet corrosion can be classified under any of eight headings, namely:

- Galvanic or bimetallic corrosion
- Uniform or general attack
- Crevice corrosion
- Pitting corrosion
- Intergranular corrosion
- Stress corrosion cracking
- Corrosion fatigue
- Selective corrosion (castings and free-matching stainless steels)

Galvanic Corrosion. When two dissimilar metals (or alloys) are immersed in a corrosive or conductive solution an electrical potential or potential difference usually exists between them. If the two metals are electrically connected then, because of this potential difference, a flow of current occurs. As the corrosion process is an electrochemical phenomenon and dissolution of a metal involves electron flow the corrosion rates for the two metals is affected. Generally, the corrosion rate for the least corrosion resistant is enhanced while that of the more corrosion resistant is diminished. In simple electrochemical terms, the least resistant metal has become anodic and the more resistant cathodic. This, then, is galvanic or dissimilar metal corrosion.

The magnitude of the changes in corrosion rates depends on the so-called electrode potentials of the two metals; the greater the difference, the greater the enhancement or diminution of the corrosion rates. It is possible to draw up a table of some commercial alloys that ranks them in order of their electrochemical potential. Such a table is known as the galvanic series. A typical one as shown in Table 3 is based on work undertaken by the International Nickel Company (now INCO Ltd.) at their Harbor Island, NC, test facility. This galvanic series relates to tests in unpolluted seawater, although different environments could produce different results and rankings. When coupled, individual metals and alloys from the same group are unlikely to show galvanic effects that will cause any change in their corrosion rates.

The problem of dissimilar metal corrosion, being relatively well understood and appreciated by engineers, is usually avoided in plant construction and in the author's experience, few cases have been encountered. Probably the most common form of unintentional galvanic corrosion is on service lines where brass fittings are used on steel pipelines—the steel suffering an increase in corrosion rate at the bimetallic junction.

One of the worst bimetallic combinations is aluminum and copper. An example of this is in relation to aluminum milk churns used to transport whey from Gruyere cheese manufacture (in Switzerland), where copper is used for the cheesemaking vats and the whey picks up traces of this metal. The effect on the aluminum churns which are internally protected with lacquer that gets worn away through mechanical damage is pretty catastrophic.

Another, somewhat unique, example of galvanic corrosion is related to a weld repair on a 304 stainless-steel storage vessel. Welding consumables containing molybdenum had been employed to effect the repair, and although it is most unusual for the potential difference between molybdenum and nonmolybdenum containing stainless steels to be sufficient to initiate galvanic corrosion, the environmental factors in this particular case were obviously such that corrosion was initiated (Fig. 5). As stated, this is somewhat unique and it is not uncommon for 316 welding consumables to be used for welding 304 stainless steel with no adverse effects. As a practice, however, it is to be deprecated and the correct welding consumables should always be employed.

Not all galvanic corrosion is bad; indeed, galvanic corrosion is used extensively to protect metal and structures by the use of a sacrificial metal coating. A classic example is the galvanizing of sheet steel and fittings, the zinc coating being applied not so much because it does not corrode, but because it does. When the galvanizing film is damaged, the zinc galvanically protects the exposed steel and inhibits rusting. Similarly, sacrificial anodes are fitted to domestic hot water storage tanks to protect the tank.

Table 3. The Galvanic Series of Some Commercial Metals and Alloys in Clean Seawater

↑	Platinum
	Gold
	Graphite
	Titanium
Noble or cathodic	Silver
	Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)
	Hastelloy C (62 Ni, 17 Cr, 15 Mo)
	18/8 Mo stainless steel (passive)
	18/8 stainless steel (passive)
	Chromium stainless steel 11–30% Cr (passive)
	Inconel (passive) (80 Ni, 13 Cr, 7 Fe)
	Nickel (passive)
	Silver solder
	Monel (70 Ni, 30 Cu)
	Cupronickels (60–90 Cu, 40–10 Ni)
	Bronzes (Cu-Sn)
	Copper
	Brasses (Cu-Zn)
	Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)
	Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
	Inconel (active)
	Nickel (active)
	Tin
	Lead
	Lead-tin solders
	18/8 Mo stainless steel (active)
	18/stainless steel (active)
	Ni-resist (high-Ni cast iron)
	Chromium stainless steel, 13% Cr (active)
	Cast iron
Active or anodic	Steel or iron
	2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)
	Cadmium
	Commercially pure aluminum (1100)
↓	Zinc
	Magnesium and magnesium alloys

Uniform or General Attack.

As the name implies, this form of corrosion occurs more or less uniformly over the whole surface of the metal exposed to the corrosive envi-

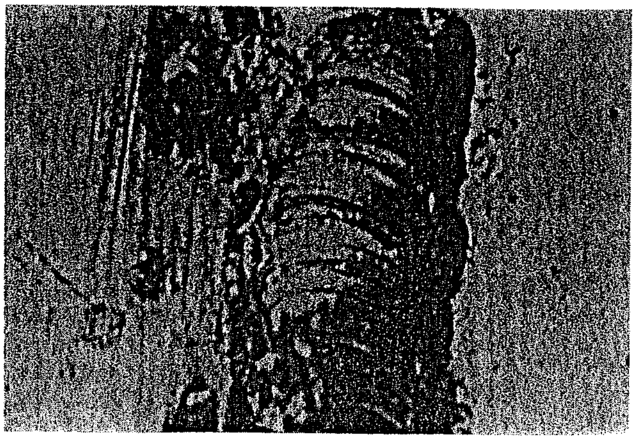

Figure 5. Galvanic corrosion of 304 stainless steel initiated by a 316 weld deposit. Note the large pit associated with the weld splatter.

ronment. It is the most common form of corrosion encountered with the majority of metals, a classic example being the rusting of carbon steel. Insofar as the corrosion occurs uniformly, corrosion rates are predictable and the necessary corrosion allowances built into any equipment. In the case of stainless steels, this form of corrosion is rarely encountered. Corrodents likely to produce general attack of stainless steel are certain mineral acids, some organic acids, and high-strength caustic soda at concentrations and temperatures well in excess of those ever likely to be found in the food industry. The same remark applies to cleaning acids such as nitric, phosphoric, and citric acids, but not for sulfuric or hydrochloric acids, both of which can cause rapid, general corrosion of stainless steels. Hence, they are not recommended for use, especially where corrosion would result in a deterioration of the surface finish of process equipment.

The behavior of both 304 and 316 stainless steels when subjected to some of the more common acids that are encountered in the food industry is graphically illustrated in Figure 6. These isocorrosion graphs, ie, lines that define the conditions of temperature and acid concentration that will produce a constant corrosion rate expressed in mils (0.001 in.) or mm loss of metal thickness per year, are used extensively by corrosion engineers in the material selection process when the form of corrosion is general attack. *They are of no value whatsoever when the corrosion mode is one of the other forms that will be defined, such as pitting or crevice corrosion.*

Crevice Corrosion. This form of corrosion is an intense local attack within crevices or shielded areas on metal surfaces exposed to corrosive solutions. It is characteristically encountered with metals and alloys that rely on a surface oxide film for corrosion protection, eg, stainless steels, titanium, aluminum.

The crevices can be inherent in the design of the equipment (eg, plate heat exchangers) or inadvertently created by bad design. Although crevice corrosion can be initiated at metal-to-metal surfaces (see Fig. 7), it is frequently encountered at metal to nonmetallic sealing faces. Any nonmetallic material that is porous and used, for example,as a gasket, is particularly good (or bad!) for initiating this form of attack. Fibrous materials that have a strong wicking action are notorious in their ability to initiate crevice attack. Similarly, materials that have poor stress relaxation characteristics, ie, have little or no ability to recover their original shape after being deformed, are also crevice creators, as are materials that tend to creep under the influence of applied loads and/or at elevated temperatures. Although used for gasketing, PTFE suffers both these deficiencies. On the other hand, elastomeric materials are particularly good insofar as they exhibit elastic recovery and have the ability to form a crevice-free seal. However, at elevated temperatures, many rubbers harden and in this condition, suffer the deficiencies of many nonelastomeric gasketing materials.

Artificial crevices can also be created by the deposition of scale from one of the process streams to which the metal is exposed. It is necessary, therefore, to maintain food processing equipment in a scale-free condition, especially on surfaces exposed to service fluids such as services side hot/cold water, cooling brines, which tend to be overlooked during plant cleaning operations.

Much research work has been done on the geometry of crevices and the influence of this on the propensity for the initiation of crevice corrosion (9). However, in practical terms, crevice corrosion usually occurs in openings a few tenths of a millimeter or less and rarely is encountered where the crevice is greater than 2 mm (0.08 in.).

Until the 1950s, crevice corrosion was thought to be due to differences in metal ion or oxygen concentration within the crevice and its surroundings. While these are factors in the initiation and propagation of crevice corrosion, they are not the primary cause. Current theory supports the view that through a series of electrochemical reactions and the geometrically restricted access into the crevice, migration of cations, chloride ions in particular, occurs. This alters the environment within, with a large reduction in pH and an increase in the cations by a factor of as much as 10. The pH value can fall from a value of, say, 7 in the surrounding solution to as low as pH 2 within the crevice. As corrosion is initiated, it proceeds in an autocatalytic manner with all the damage and metal dissolution occurring within the crevice and little or no metal loss outside. The confined and autocatalytic nature of crevice corrosion results in significant loss of metal under the surface of site of initiation. As a result, deep and severe undercutting of the metal occurs (see Fig. 8). The time scale for initiation of crevice corrosion can vary from a few hours to several months and, once initiated, can progress very rapidly. Stopping the corrosion process can be extremely difficult as it is necessary to remove all the trapped reactants and completely modify the occluded environment. The difficulty of attaining this will be appreciated by reference to Figure 8, where the entrance to the corroded region is only 0.5 mm (0.020 in.).

While methods for combating the onset of crevice corrosion can be deduced from the foregoing text, a reiteration of some of the more important precautions is not out of place, viz:

- Good-quality, crevice-free welded joints are always preferable to bolted joints
- Good equipment design (well-designed gasket sealing faces) that avoids unintentional crevices and does not permit the development of stagnant regions
- Frequent inspection of equipment and removal of surface deposits
- Use of good-quality rubber gaskets rather than absorbent packings
- Good gasket maintenance; replacement when hardened or damaged

However, certain pieces of equipment are by virtue of their design highly creviced. In such cases, it is necessary to recognize the potential corrosion risk and select the materials of construction that will resist the initiation of crevice corrosion by the environment. Similarly, cleaning and sanitizing regimes must be developed to avoid the onset of attack

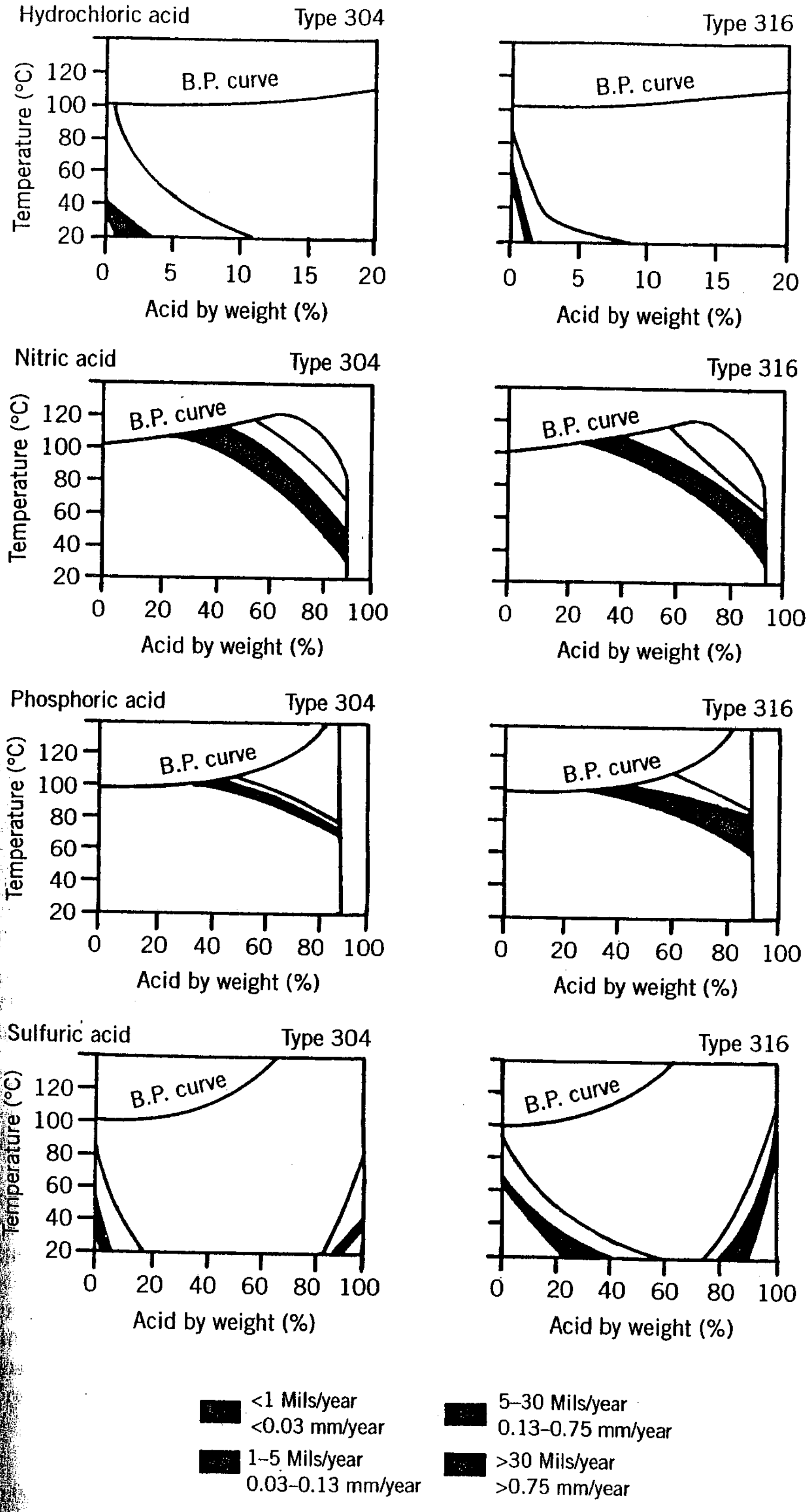

Figure 6. Corrosion resistance of 304 and 316 stainless steels to mineral acids. *Source:* Reproduced by permission of British Steel Plc.

In the case of stainless steels, although there are several ionic species that will initiate the attack, by far the most common are solutions containing chloride. The presence of salt in virtually all foodstuffs highlights the problem. Low pH values also enhance the propensity for initiation of attack.

Other environmental factors such as temperature and the oxygen or dissolved air content of the process stream all play a role in the corrosion process.

Because the presence of oxygen is a prerequisite for the onset of crevice corrosion (and many other forms of attack), in theoretical terms complete removal of oxygen from a

Figure 7. Crevice corrosion at the interplate contact points of a heat-exchanger plate.

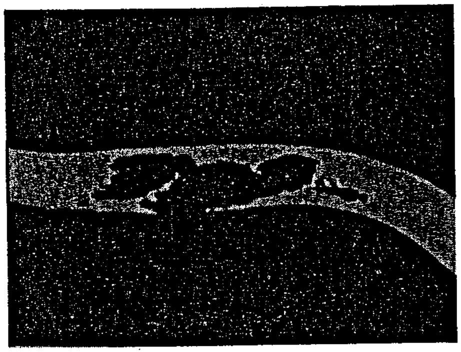

Figure 8. Photomicrograph of a section through a site of crevice corrosion. Note the deep undercutting which is typical of chloride-induced attack on stainless steel.

process stream will inhibit corrosion. In practice, however, this is difficult to achieve. Only in equipment where complete and effective deaeration occurs, such as a multiple effect evaporator operating under reduced pressure, will the beneficial effect of oxygen removal be achieved.

Stainless steels containing molybdenum (316, 317) have a much higher resistance to crevice corrosion than do alloys without this element (304, 321, 347). The higher the molybdenum content, the greater the corrosion resistance. For particularly aggressive process streams, titanium is often the only economically viable material to offer adequate corrosion resistance.

Pitting Corrosion. As the name implies, pitting is a form of corrosion that leads to the development of pits on a metal surface. It is a form of extremely localized but intense attack, insidious insofar as the actual loss of metal is negligible in relation to the total mass of metal that may be affected. Nevertheless, equipment failure by perforation is the usual outcome of pitting corrosion. The pits can be small and sporadically distributed over the metal surface (Fig. 9) or extremely close together, close enough, in fact, to give the appearance of the metal having suffered from general attack.

In the case of stainless steels, environments that will initiate crevice corrosion will also induce pitting. As far as the food industry is concerned, it is almost exclusively caused by chloride containing media, particularly at low pH values.

Many theories have been developed to explain the cause of initiation of pitting corrosion (10), and the one feature they have in common is that there is a breakdown in the passive oxide film. This results in ionic migration and the development of an electrochemical cell. There is, however, no unified theory that explains the reason for the film breakdown. Evans (11) for example, suggests that metal dissolution at the onset of pitting may be due to a surface scratch, an emerging dislocation or other defects, or random variations in solution composition. However, propagation of the pit proceeds by a mechanism similar to that occurring with crevice corrosion. Like crevice corrosion, the pits are often undercut and on vertical surfaces may assume an elongated morphology due to gravitational effects (Fig. 10).

The onset of pitting corrosion can occur in a matter of days but frequently requires several months for the development of recognizable pits. This makes the assessment of the pitting propensity of a particular environment very difficult to determine, and there are no short-cut laboratory testing techniques available. Methods and test solutions are available to rank alloys; the best known and most frequently quoted is ASTM Standard G48 (12), which employs 6% ferric chloride solution. Another chemical method involving ferric chloride determines the temperature at

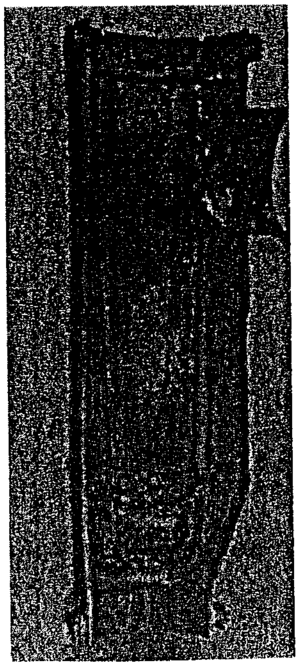

Figure 9. Pitting corrosion of a stainless-steel injector caused by the presence of hydrochloric acid in the steam supply.

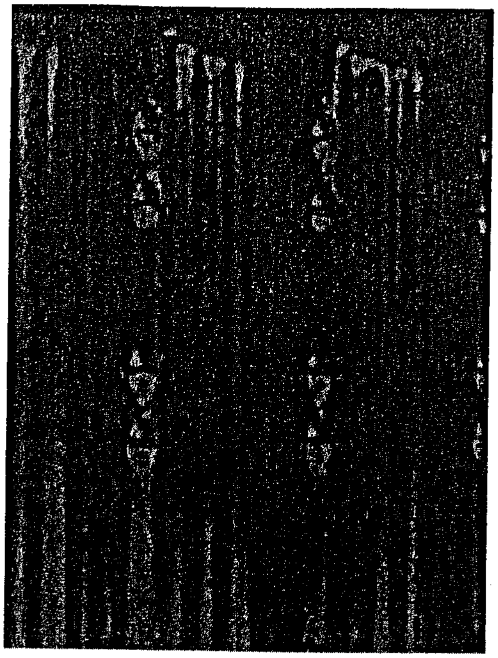

Figure 10. Elongated pitting attack on a 316 stainless-steel heat exchanger plate.

which the solution will cause pitting within a 24-h test period, the results being expressed as the critical pitting temperature or CPT (13). However, as stated, both of these methods are used to rank the susceptibility of a range of alloys rather than define the performance of a material in a service environment. Electrochemical methods have also been used.

As with crevice corrosion, alloy composition has a profound effect on the resistance of a material to pitting attack. Greene and Fontana (14) summarized the effect of various elements as shown in Table 4.

Intergranular Corrosion. A fact not often appreciated is that metals and alloys have a crystalline structure. However, unlike crystalline solids such as sugar or salt, metallic crystals can be deformed or bent without fracturing; in other words, they are ductile. In the molten state, the atoms in a metal are randomly distributed but on cooling and solidification, they become arranged in crystalline form. Because crystallization occurs at many points in the solidification process, these crystals or grains are randomly orientated and the region where they meet are grain boundaries. In thermodynamic terms, the grain boundaries are more susceptible to corrosion attack because of their higher free energy, although in practice the difference in free energy of the grain boundaries and the main crystals or grains in a homogeneous alloy are too small to be significant. However, when the metal or alloy has a heterogeneous structure, preferential attack at or adjacent to the grain boundaries can occur. This is intergranular corrosion as shown in Figure 11.

When austenitic stainless steels are heated to and held in the temperature range of 600–900°C (1100–1650°F), the material becomes sensitized and susceptible to grain boundary corrosion. It is generally agreed that this is due to chromium combining with carbon to form chromium carbide, which is precipitated at the grain boundaries. The net effect is that the metal immediately adjacent to the grain boundaries is denuded of chromium and instead of having a composition of, say, 18% chromium and 8% nickel, it may assume an alloy composition where the chromium content is reduced to 9% or even lower. As such, this zone depleted in chromium bears little similarity to the main metal matrix and has lost one of the major alloying elements on which it relied for its original corrosion resistance. Indeed, the lowering of corrosion resistance in this zone is so great that sensitized materials are subject to attack by even mildly corrosive environments.

As supplied from the steel mills, stainless steels are in the so-called solution annealed condition, ie, the carbon is in solution and does not exist as grain boundary chromium carbide precipitates. During fabrication where welding is involved, the metal adjacent to the weld is subjected to temperatures in the critical range (600–900°C/1100–1650°F) where sensitization can occur. As such, therefore, this zone may be susceptible to the development of intergranular carbide precipitates. Because the formation of chromium carbides is a function of time, the longer the dwell time in the critical temperature zone, the greater the propensity for carbide formation. Hence, the problem is greatest with thicker metal sections due to the thermal mass and slow cooling rate.

By heating a sensitized stainless steel to a temperature of 1050°C (1950°F), the carbide precipitates are taken into solution and by rapidly cooling or quenching the steel from this temperature, the original homogeneous structure is reestablished and the original corrosion resistance restored.

The first stainless steels were produced with carbon contents of up to 0.2% and as such, were extremely susceptible to sensitization and in-service failure after welding. In consequence, the carbon levels were reduced to 0.08%, which represented the lower limit attainable with steel making technology then available. Although this

Table 4. The Effect of Alloying on Pitting Resistance of Stainless-Steel Alloys

Element	Effect on pitting resistance	Element	Effect on pitting resistance
Chromium	Increases	Molybdenum	Increases
Nickel	Increases	Nitrogen	Increases
Titanium/Niobium	No effect in media other than ferric chloride	Sulfur (and selenium)	Decreases
Silicon	Decrease or increase depending on the absence or presence of molybdenum	Carbon	Decreases if present as grain boundary precipitates

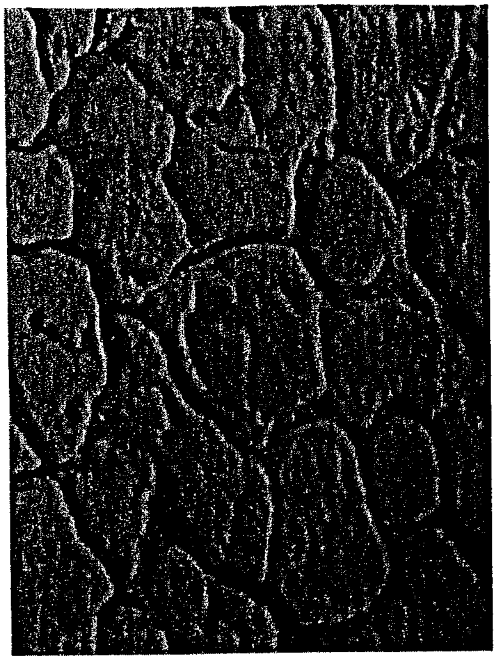

Figure 11. Scanning electron micrograph of the surface of sensitized stainless steel showing preferential attack along the grain boundaries.

move alleviated the problem, it was not wholly successful, particularly when welding thicker sections of the metal. Solution annealing of the fabricated items was rarely a practical proposition and there was a need for a long-term solution. It was shown that titanium or niobium (columbium) had a much greater affinity for the carbon than chromium and by additions of either of these elements, the problem was largely overcome. The titanium or niobium carbides that are formed remain dispersed throughout the metal structure rather than accumulating at the grain boundaries.

Grade 321 is a type 304 (18 Cr, 8 Ni) with titanium added as a stabilizing element, while grade 347 contains niobium. By far, the most commonly used is 321, grade 347 being specified for certain chemical applications.

Modern steelmaking techniques such as AOD (air-oxygen decarburization) were developed to reach even lower levels of carbon, typically less than 0.03%, to produce the "L" grades of stainless steel. These are commercially available and routinely specified where no sensitization can be permitted. With these advances in steel making technology, even the standard grades of stainless steels have typically carbon levels of 0.04–0.05% and, generally speaking, are weldable without risk of chromium carbide precipitates at metal thicknesses of up to 6 mm (1/4 in.). Above this figure or where multipass welding is to be employed, the use of a stabilized or "L" grade is always advisable.

Stress Corrosion Cracking. One of the most insidious forms of corrosion encountered with the austenitic stainless steels is stress corrosion cracking (SCC). The morphology of this type of failure is invariably a fine filamentous crack that propagates through the metal in transgranular mode. Frequently, the crack is highl branched as shown in Figure 12, although sometimes i can assume a single-crack form. Factors such as meta structure, environment, and stress level have an effect o crack morphology. The disturbing feature of SCC is tha there is virtually no loss of metal and frequently, it is no visible by casual inspection and is only apparent after pe foration occurs. Some claim that as much as 50% of th failures of stainless steel are attributable to this cause.

Another characteristic of SCC in stainless steels is tha once detected, repair by welding is extremely difficul Crack propagation frequently occurs below the surface the metal, and any attempt to weld repair results in th crack opening up and running ahead of the welding torc The only practical method of achieving a satisfactory repair is to completely remove the affected area with a 15 25 cm (6–9 in.) allowance all around the area of visibl damage and replace the section. Even then, there is n guarantee that the damaged zone has been entirely removed. In most cases, there are three prerequisites for th initiation of SCC.

- *Tensile Stress.* This may be either residual stres from fabricating operations or applied through th normal operating conditions of the equipment. Furthermore, it has been observed that a corrosion pi can act both as a stress raiser and a nucleation sit for SCC.

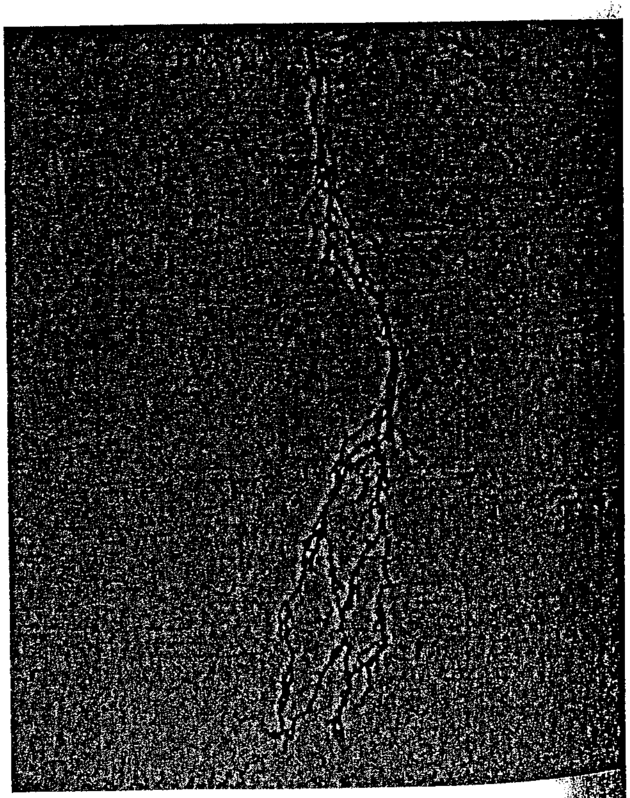

Figure 12. Photomicrograph of a typical stress corrosion showing its highly branched morphology and transgranul agation.

- *Corrosive Species.* Although there are a number of ionic compounds that will act as the corrodent, in the food industry this invariably is the chloride ion. High-strength caustic soda at elevated temperatures will also induce SCC, but the concentrations and temperatures required are well in excess of those ever likely to be encountered. Furthermore, the crack morphology is inter- rather than transgranular. pH also plays a role and generally speaking, the lower the pH the greater the propensity for SCC.
- *Temperature.* It generally is regarded by many that a temperature in excess of 60°C (140°F) is required for this type of failure, although the author has seen examples occurring at 50°C (122°F) in liquid glucose storage vessels.

In the absence of any one of these prerequisites, the initiation of SCC is eliminated. Therefore, it is worth considering the practical approach to its elimination from equipment.

Figure 13 is a diagrammatic representation of the effect of stress on "time-to-failure." As will be seen, by reducing the stress level below a certain critical point, the "time-to-failure" can be increased by several orders of magnitude. On small pieces of equipment, residual stress from manufacturing operations can be removed by stress-relief annealing, which, in the case of stainless steels, is the same as solution annealing. For large pieces of equipment such as storage vessels this approach is clearly impractical. Applied stress is very much a function of the operational conditions of the equipment and only by reducing the stress level by increasing the thickness of the metal can this be reduced. However, this too is a somewhat impractical and uneconomic approach. Some (15) claim that by placing the surface of the metal under compressive rather than tensile stress, by shot peening with glass beads, the problem of SCC can be minimized or eliminated. This too is not a practical proposition for many items of food processing equipment.

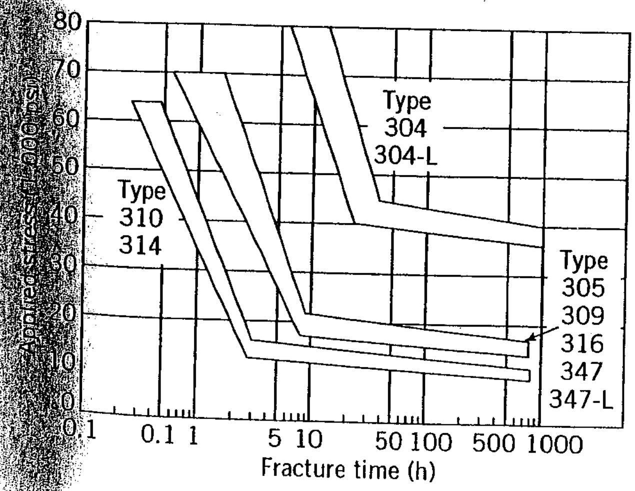

Figure 13. Composite curves illustrating the relative resistance to stress corrosion cracking of some commercial stainless steel in a specific test solution.

As for the matter of corrosive species, it is questionable if anything can be done about elimination. With foodstuffs, for example, this invariably will be the chloride ion, a naturally occurring or essential additive.

Similarly, little can be done in respect to the temperature as this is going to be essential to the processing operation.

As shown by Copson (16), the tendency for iron-chromium-nickel alloys to fail by SCC in a specific test medium (boiling 42% magnesium chloride solution) is related to the nickel content of the alloy. Figure 14 shows this effect, and it is unfortunate that stainless steels with a nominal 10% nickel have the highest susceptibility to failure. Increasing the nickel content of the alloy results in a significant increase in the time-to-failure, but of course, this approach incurs not only the increased cost of the nickel but also the added penalty of having to increase the chromium to maintain a balanced metallurgical structure. The more effective approach is by reducing the nickel content of the alloy.

A group of stainless steels have been developed that exploit this feature, and although their composition varies from producer to producer, they have a nominal composition of 20/22% chromium, 5% nickel. Molybdenum may or may not be present, depending on the environment for which the alloy has been designed. These alloys differ from the austenitic stainless steels insofar as they contain approximately 50% ferrite; hence their designation, austenitic-ferritic, or more commonly, duplex stainless steels. It is only with the advent of modern steel making technology, particularly in relation to the lower carbon levels that can be achieved, that these alloys have become a

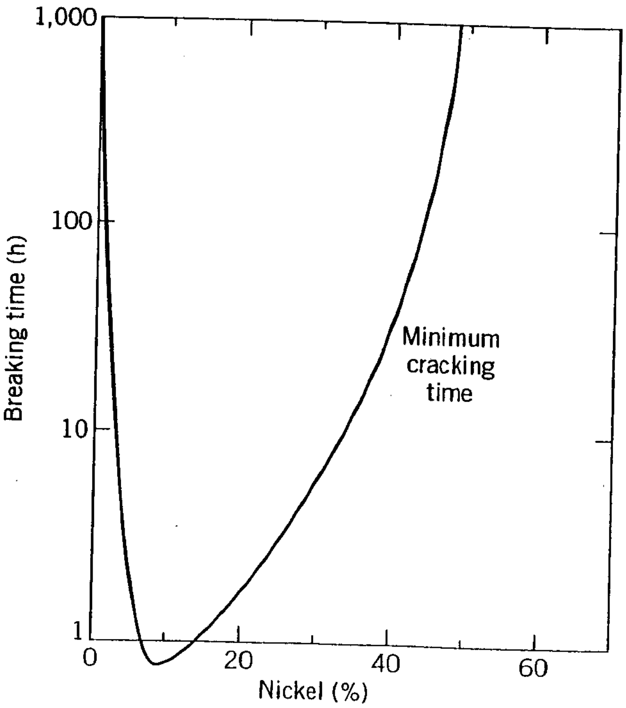

Figure 14. Stress corrosion cracking of iron, chromium, nickel alloys—the Copson curve. Data points have been omitted for clarity.

commercially viable proposition. Because of their low carbon content, typically 0.01–0.02%, the original problems associated with welding ferritic stainless steels and chromium carbide precipitation have been overcome. The alloys are almost twice as strong as the austenitic stainless steels and are ductile and weldable. From a general corrosion standpoint, they are comparable with, or marginally superior to, their 300 series equivalent; but from an SCC standpoint in test work and from field experience, they offer a resistance orders of magnitude better.

Also now available are fully ferritic stainless steels such as grade 444, which contains 18% chromium and 2% molybdenum. This alloy contains carbon at the 0.001% level and therefore does not suffer the problems of welding that were encountered with the original ferritic steels. Furthermore, stabilizing elements such as titanium and niobium are also alloying additions that minimize the tendency for intergranular chromium carbide formation. The main disadvantage of these materials is their susceptibility to grain growth during welding (Fig. 15), which makes them extremely sensitive to fracture even at room temperature. Welding sections thicker than 3 mm (1/8 in.) are not regarded as a practical proposition, and, therefore, their use tends to be limited to tubing.

Corrosion Fatigue. Fatigue is not a form of corrosion in the accepted sense as there is no loss of metal, but can be associated with other forms of localized attack. Because pure fatigue is an *in vacuo* phenomenon, a more correct term is corrosion fatigue or environmental cracking, which is the modern expression and takes into account cracking where the corrosive factor has played a major role on the crack morphology.

The primary cause of corrosion fatigue is the application of fluctuating pressure loads to components that, while of adequate design to withstand normal operating pressures eventually fail under the influence of cyclic loading. The components can be of extremely rigid construction such as a homogenizer block or of relatively light construction such as pipework. There are many potential sources of the fluctuating pressure, the most common of which are positive-displacement pumps (eg, homogenizer or metering pumps), rapid-acting on-off valves that will produce transient pressure peaks, frequent stop-start operations, dead ending of equipment linked to a filling machine, etc.

Figure 15. Photomicrograph of a weld deposit on a ferritic stainless steel. Compare the size of grains in the weld with those in the parent material on the left.

Generally speaking, fatigue cracks are straight, withou branching and without ductile metal distortion of th material adjacent to the crack. The one characteristic o fatigue cracks is that the crack face frequently has series of conchoidal markings that represent the stepwis advance of the crack front (Fig. 16). Although, as stated corrosion fatigue cracks are generally straight and unbranched, where fatiguing conditions pertain in a potentially corrosive environment, the influence of the corrosiv component may be superimposed on the cracks. This ca lead to branching of the cracks, and in the extreme case the crack may assume a highly branched morpholog which is almost indistinguishable from stress corrosio cracking. It is only when the crack face is examined unde high-power magnification that it is possible to categoriz the failure mode. An example of this is shown in Figur 17, which has all the features of stress corrosion crackin but the scanning electron micrograph (Fig. 18) clearl shows the stepwise progression of the crack front.

The site for initiation of corrosion fatigue is frequentl a discontinuity in the metal section of the component. Thi may be, for example, a sharp change in diameter of a shaf where inadequate radiusing of the diametric change results in a high cycle stress level through shaft rotation an thus an initiation point for fatigue. A corrosion pit, whic under cyclic loading will have a high stress-level association, can also act as a nucleation site (epicenter) for fatigu failure. Because of the corrosive element, it is sometime difficult to establish whether the pit and associated corrosion were the initiating mechanism for the cracking o the result of corrosion superimposed on a crack, the fra

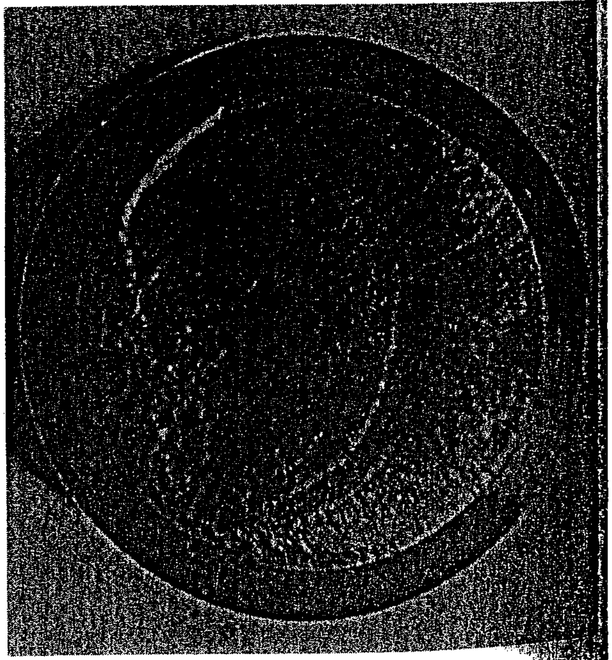

Figure 16. Fatigue cracking of a 1-in.-diameter stainless steel bolt showing the characteristic conchoidal striations on the crack face.

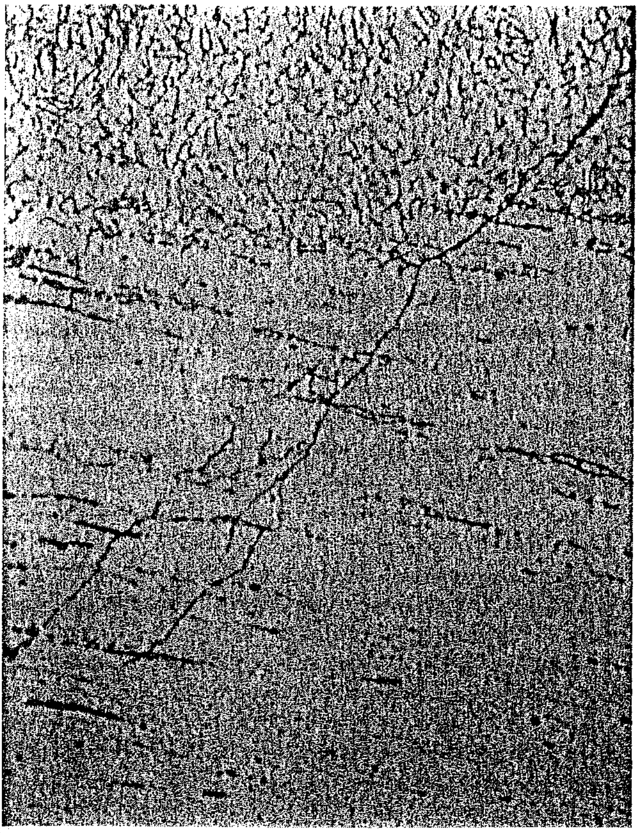

Figure 17. Photomicrograph of a fatigue crack showing all the features of stress corrosion cracking. Compare this with Figure 12.

Figure 18. Scanning electron micrograph of the fracture face of the crack shown in Figure 17. Note the stepwise progression of the crack.

ture face of which will be in an "active" state and therefore more susceptible to corrosion processes.

The whole subject of fatigue and corrosion fatigue is complex. However, as far as food processing equipment is concerned, avoidance of fatigue failure is best achieved by avoiding pulsing and pressure peaks. This requires the use of well-engineered valving systems and avoiding the use of positive-displacement pumps. Where this is impractical, provision should be made to incorporate pulsation dampers to smooth out the pressure peaks and minimize the risk of fatigue failures.

Selective Corrosion ***Corrosion of Castings.*** There are a number of stainless-steel components found in food processing plants such as pipeline fittings and pump impellers that are produced as castings rather than fabricated from wrought material—notably, the cast equivalents of grade 304 (CF8) and 316 (CF8M). Although the cast and wrought materials have similar, but not identical, compositions with regard to their chromium and nickel contents, metallurgically they have different structures. Whereas the wrought materials are fully austenitic, castings will contain some ferrite or more terminologically correct, δ (delta) ferrite in the basic austenitic matrix. The ferrite is necessary to permit welding to the castings, to avoid shrinkage cracking during cooling from the casting temperature, and to act as nucleation sites for the precipitation of chromium carbides, which will invariably be present as it will not always be possible to solution anneal the cast components.

The nominal ferrite level is usually 5–12%. Below 5%, cracking problems may be experienced while above 12%, the ferrite tends to form a continuous network rather than remain as isolated pools.

Because the crystallographic structures of the ferrite and austenite differ (austenite is a face-center cubic and the ferrite, body-center cubic), the ferrite has, thermodynamically speaking, a higher free energy, which renders it more susceptible to attack, particularly in low-pH chloride-containing environments such as tomato ketchup and glucose syrups. Although the problem is not so severe when the ferrite occurs as isolated pools, when present as a continuous network, propagation of the corrosion occurs along the ferrite, with the austenite phase being relatively unaffected (Fig. 19). Because the products of corrosion are not leached out from the corrosion site and are more voluminous than the metal, corroded castings frequently assume a blistered or pockmarked appearance. The common environments encountered in the industry that produce preferential ferrite attack are the same as those causing

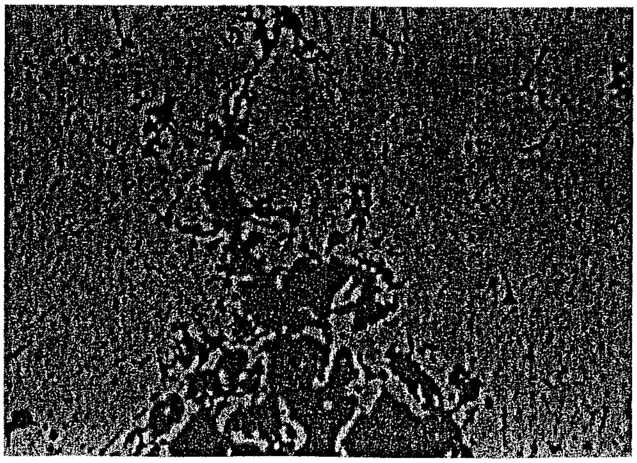

Figure 19. Photomicrograph of a section of cast 316 (CF8M) showing preferential attack of the ferrite phase.

stress corrosion cracking. Therefore, this form of damage is frequently also present (Fig. 20).

Depending on the method used to make the casting, the surface of the castings can be chemically modified, which reduces the corrosion resistance. Small components are usually cast by either the shell molding process or produced as investment castings. In the shell molding process, the sand forming the mold is bonded together with an organic resin that carbonizes when the hot metal is poured. This results in the metal adjacent to the mold having an enhanced carbon level with the formation of intergranular carbide precipitates and hence, a susceptibility to intergranular attack and other forms such as crevice, pitting, and stress corrosion cracking. Methods of overcoming this include solution annealing or machining off the carburized skin of metal.

With investment castings, the mold is made of zircon sand (zirconium silicate), and fired at a high temperature to remove all traces of organic material and wax that is used as a core in the moldmaking process. They do not, therefore, have this carburized layer and offer a much better resistance to surface corrosion.

Free-Machining Stainless Steels. Stainless steels are notoriously difficult to machine, especially turning, not so much because they are hard, but because the swarf tends to form as continuous lengths that clog the machine and to weld to the tip of the machine tools. One method of overcoming this is to incorporate a small amount, typically 0.2%, of sulfur or selenium in the alloy. These elements react with the manganese to form manganese sulfide or selenide, which, being insoluble in the steel, forms as discrete pools in castings or as elongated, continuous stringers in, say, wrought bar. The effect of the sulfide inclusions is to cause the material to form chips rather than long strings of swarf when being machined. Both manganese sulfide and selenide have virtually zero corrosion resistance to dilute mineral acids or other corrosive media. Thus, the free-cutting variants have a much lower corrosion resistance than their designation would imply. Indeed, some believe that the addition of sulfur to a type 316 material will offset the beneficial effect of the alloying addition of molybdenum. As stated, the sulfide inclusions will occur in castings as discrete pools, and therefore there will not be a continuous corrosion path. However, one of the products of corrosion in acidic media will be hydrogen sulfide, which has a profound effect on the corrosivity of even dilute mineral acids, causing attack of the austenitic matrix.

In the case of wrought materials, in particular bar stock, the sulfide inclusions are present as semicontinuous stringers and can suffer so-called end-grain attack in mildly corrosive media.

Stainless-steel nuts and bolts, which are produced on automatic thread-cutting machines, are invariably made from free-cutting materials. Figure 21 illustrates the difference in corrosion resistance of a bolt made from this and a nonfree machining 316. Both bolts were exposed to the same mildly acidic environment.

When specifying materials of construction, quite clearly due cognizance of this difference must be recognized. Any components turned from bar stock which are likely to come into contact with potentially corrosive environments should always be specified in 316 and not in the free machining, sulfur-containing variant.

CORROSION OF SPECIFIC ENVIRONMENTS

From a corrosion standpoint, the environments likely to be encountered in the food industry that may cause premature equipment failure may be classified under main headings:

Noncorrosive
Mildly corrosive
Highly corrosive
Service fluids
Alkaline detergents
Acidic detergents
Sanitizing agents

Noncorrosive Foodstuffs

In general terms, natural foodstuffs such as milk, cream, natural fruit juices, and whole egg do not cause corrosion.

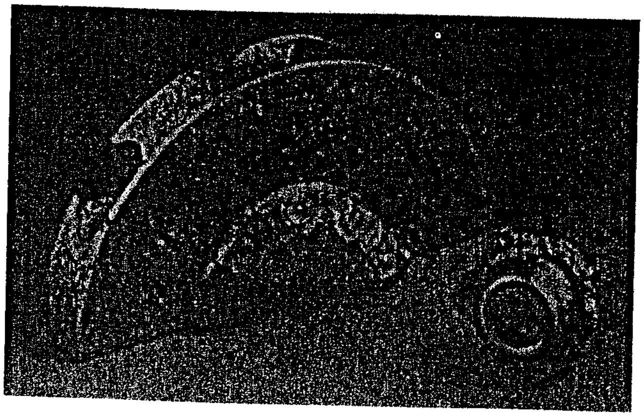

Figure 20. Corroded pump impeller (above) and valve body (below) caused by tomato ketchup. Note the pocklike corrosion sites.

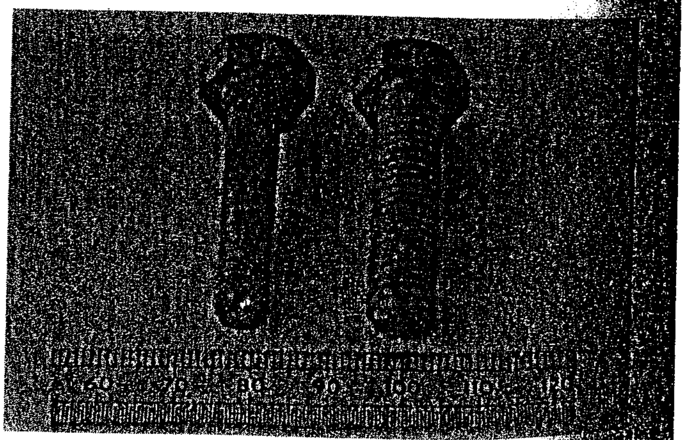

Figure 21. Free machining and nonfree machining bolts after immersion in a mildly acidic environment.

problems with 304 or 316 stainless steels. Prepared foodstuffs to which there is no added salt such as yogurt, beer, ice cream, wines, spirits, and coffee also fall within this classification. For general storage vessels, pipelines, pumps, fittings or valves, grade 304 is perfectly satisfactory. However, for plate heat exchangers that are highly creviced and therefore prone to crevice corrosion, grade 316 frequently is employed. This offers a higher degree of protection against some of the more acidic products such as lemon juice, which may contain small quantities of salt and also provides a higher level of integrity against corrosion by service liquids and sanitizing agents.

It is quite common to use sulfur dioxide or sodium bisulfite for the preservation of fruit juices and gelatin solutions and in such cases, storage vessels always should be constructed from 316. Although the sulfur dioxide is noncorrosive at ambient temperature in the liquid phase, as a gas contained in significant quantities within the head space in a storage tank it tends to dissolve in water droplets on the tank wall. In the presence of air, the sulfurous acid that forms is oxidized to sulfuric acid at a concentration high enough to cause corrosion of 304 but not of 316.

Mildly Corrosive Foodstuffs

This category of foodstuffs covers products containing relatively low levels of salt and where pH values are below 7. Examples include glucose/fructose syrups and gelatin, the production of which may involve the use of hydrochloric acid. For storage vessels, pipelines, fittings, and pumps, grade 316 has established a good track record, and boiling pans in this grade of steel are perfect for long and satisfactory service. The corrosion hazards increase however in processing operations involving high temperatures and where the configuration of the equipment is such as to contain crevices, especially when the product contains dissolved oxygen. For example, multistage evaporators operating on glucose syrup will usually have the first stage, where temperatures may approach 100°C (212°F), constructed in a super stainless steel such as 904L. Subsequent effects where temperatures are lower and where the product has been deoxygenated may be fabricated in grade 316 stainless steel.

As previously indicated, it is common practice to use sulfur dioxide as a preservative in dilute gelatin solutions during storage prior to evaporation. In some cases, excess hydrogen peroxide will be added to neutralize the sulfur dioxide immediately before concentration. This can have a catastrophic effect on the 300 series stainless steels and indeed on even more highly alloyed metals such as 904L, because of the combined effect of the chlorides present with the excess hydrogen peroxide. Because of this, it is a more acceptable practice to make the peroxide addition after rather than before evaporation.

Gelatin for pharmaceutical end use is subject to UHT treatment to ensure sterility. This will involve heating the gelatin solutions to 135°C (285°F) and holding at that temperature for a short period of time. Plate heat exchangers are used extensively for this duty. Although plates made from 316 stainless steel give a reasonable life of typically 2–3 years, a corrosion resistant alloy with an enhanced-level molybdenum is to be preferred.

Highly Corrosive Foodstuffs

The list of foodstuffs falling in this category is almost endless—gravies, ketchups, pickles, salad dressings, butter, and margarine—in fact, anything to which salt has been added at the 1–3% level or even higher. Also within this category must be included cheese salting brine and other brines used in the preservation of foodstuffs that undergo pasteurization to minimize bacterial growth on food residues remaining in the brine. Although these brines are usually too strong to support the growth of common organisms, salt resistant strains (halophiles) are the major problem.

Low-pH products containing acetic acid are particularly aggressive from a corrosion standpoint, but selection of materials for handling these products depends to a great extent on the duty involved.

When trying to define the corrosion risk to a piece of equipment handling potential corrodents, several factors come into play. While temperature, oxygen content, chloride content, and pH are the obvious ones, less obvious and equally important is contact time. All three main forms of corrosion induced in stainless steels (crevice, pitting, and stress corrosion cracking) have an induction period before the onset of corrosion. This can vary from a few hours to several months depending on the other operative factors. In a hypothetical situation where stainless steel is exposed to a potentially corrosive environment, removal of the steel and removal of the corrodents will stop the induction and the status quo is established. On repeating the exposure, the induction period is the same. In other words, the individual periods the steel spends in contact with the corrodent are not cumulative and each period must be taken in isolation.

When the contact period is short, temperatures are low and a rigorous cleaning regime is implemented at the end of each processing period, 316 stainless steel will give excellent service. However, where temperatures are high and contact periods are long, the corrosion process may be initiated. This is especially so in crevices such as the interplate contact points on a plate heat exchanger where, albeit at a microscopic level, corrodents and corrosion products are trapped in pits or cracks. Geometric factors may prevent the complete removal of this debris during cleaning and under such circumstances, the corrosion process will be ongoing.

Because of the perishable nature of foodstuffs, storage is rarely for prolonged periods or at high temperatures, and regular, thorough cleaning tends to be the norm. The one exception to this is buffer storage vessels for holding "self-preserving" ketchup and sauces. For such duties, an alloy such as 904L, Avesta 254 SMO, or even Inconel 625 may be required.

While all the foregoing applies to general equipment, the one exception is plate heat exchangers. Their highly creviced configuration and the high temperatures employed render them particularly susceptible. Plates made from grade 316 have a poor track record on these types of duties. Even the more highly alloyed materials do not offer complete immunity. The only reasonably priced material that is finding increased usage in certain areas of food processing is titanium.

The fact that butter and margarine have been included in this group of corrodents requires comment. Both these foodstuffs are emulsions containing typically 16% water and 2% salt. A fact not often appreciated is that the salt is dissolved in the water phase, being insoluble in the oil. From a corrosion standpoint, therefore, the margarine or butter may be regarded as a suspension of 12% salt solution and as such is very corrosive to 316 stainless steel at the higher processing temperatures. The only mitigating feature that partly offsets their corrosivity is the fact that the aqueous salty phase is dispersed in an oil rather than the reverse and that the oil does tend to preferentially wet the steel surface and provide some degree of protection. However, the pasteurizing heat exchanger in margarine rework systems invariably has titanium plates as the life of 316 stainless steel is limited and has been known to be as little as 6 weeks.

Corrosion by Service Fluids

Steam. Because it is a vapor and free from dissolved salts, steam is not corrosive to stainless steels. Although sometimes contaminated with traces of rust from carbon steel steam lines, in the author's experience no case of corrosion due to industrial boiler steam ever has been encountered.

Water. The quality and dissolved solids content of water supplies varies tremendously, with the aggressive ionic species, chloride ions, being present at levels varying between zero, as found in the lakeland area of England, to several hundred parts per million, as encountered in coastal regions of Holland. It is also normal practice to chlorinate potable water supplies to kill pathogenic bacteria with the amount added dependent on other factors such as the amount of organic matter present. However, most water supply authorities aim to provide water with a residual chlorine content of 0.2 ppm at the point of use. Well waters also vary in composition depending on the geographical location, especially in coastal regions where the chloride content can fluctuate with the rise and fall of the tide.

What constitutes a "good" water? From a general user viewpoint, the important factor is hardness, either temporary hardness caused by calcium and magnesium bicarbonates that can be removed by boiling, or permanent hardness caused by calcium sulfate that can be removed by chemical treatment. While hardness is a factor, chloride content and pH probably are the most important from a corrosion standpoint.

What can be classed as a noncorrosive water supply from a stainless-steel equipment user? Unfortunately, there are no hard-and-fast rules that will determine whether corrosion of equipment will occur. As has been repeatedly stated throughout this article, so many factors come into play. The type of equipment, temperatures, contact times, etc all play a role in the overall corrosion process. Again, as has been stated before, the most critical items of equipment are those with inherent crevices—evaporators and plate heat exchangers among others. Defining conditions of use for this type of equipment will be the regulatory factor. Even then, it is virtually impossible to define the composition of a "safe" water, but as a general guideline, water with less than 100 ppm chloride is unlikely to initiate crevice corrosion of type 316 stainless steel while a maximum level of 50 ppm should be used with type 304.

Cooling tower water systems are frequently overlooked as a potential source of corrodents. It must be appreciated that a cooling tower is an evaporator, and although the supply of makeup water may contain only 25 ppm chloride, over a period of operation this can increase by a factor of 10 unless there is a routine bleed on the pond.

Water scale deposits formed on heat-transfer surfaces should always be removed as part of the routine maintenance schedule. Water scale deposits can accumulate chloride and other soluble salts that tend to concentrate, producing higher levels in contact with the metal than indicated by the water composition. Furthermore, water scale formed on a stainless-steel surface provides an ideal base for the onset of crevice corrosion.

As stated previously, potable water supplies usually have a residual free chlorine content of 0.2 ppm. Where installations have their own private wells, chlorination is undertaken on site. In general terms, the levels employed by the local water authorities should be followed and overchlorination avoided. Levels in excess of 2 ppm could initiate crevice corrosion.

Cooling Brines. Depending on the industry, these can be anything from glycol solutions, sodium nitrate/carbonate, or calcium chloride. It is the latter which are used as a 25% solution that can give rise to corrosion of stainless steel unless maintained in the ideal condition, especially when employed in the final chilling section of plate heat exchangers for milk and beer processing. However, by observing certain precautions, damage can be avoided.

The corrosion of stainless steels by brine can best be represented as shown in Figure 22. It will be noted that an exponential rise in corrosion rate with reducing pH occurs in the range pH 12-7. The diminution in number of pits occurring in the range pH 6-4 corresponds with the change in mode of attack, ie, from pitting to general corrosion. It will be seen that ideally the pH of the solution should be maintained in the region 14-11. However, calcium chloride brine undergoes decomposition at pH values higher than 10.6:

$$CaCl_2 + 2NaOH \rightarrow Ca(OH)_2\downarrow + 2NaCl$$

Scale deposition occurs and heat-transfer surfaces become fouled with calcium hydroxide scale. Furthermore, the scale that forms traps quantities of chloride salts that cannot be effectively removed and remain in contact with the equipment during shutdown periods. This is particularly important in equipment such as plate heat exchangers that are subjected to cleaning and possibly hot-water sterilization cycles at temperatures of 80°C (176°F) or higher.

The other aspect, nonaeration, is equally important. Air contains small quantities of carbon dioxide that form a slightly acidic solution when dissolved in water. This has

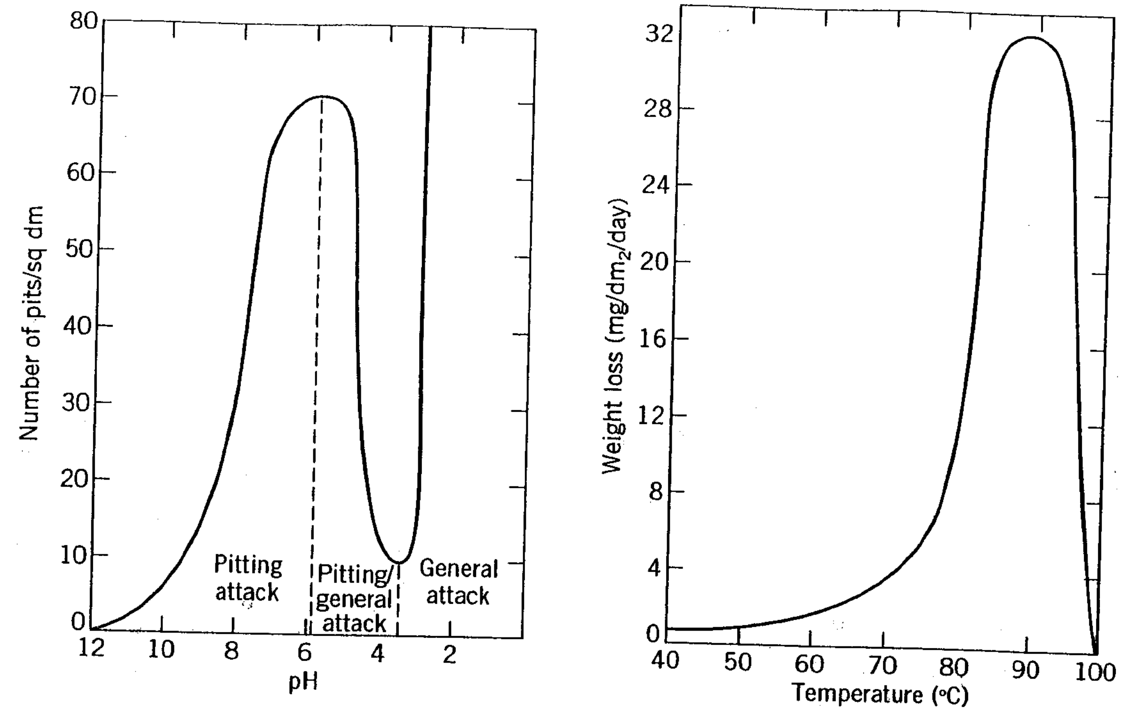

Figure 22. The effect of pH and temperature on the pitting of stainless steel by brine.

the effect of neutralizing the buffering action of any alkaline components in the brine:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

$$Na_2CO_3 + CaCl_2 \rightarrow 2NaCl + CaCO_3\downarrow$$

or

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

Therefore, the pH of the brine decreases and assumes a value of about pH 6.5, which is the region where pitting incidence is highest. Furthermore, scale deposits of calcium carbonate are laid down on heat-transfer surfaces, creating the problems referred to above.

The precautions to be observed when using brine circuits are

- Ensure correct pH control and maintain in the range pH 9.5–10.
- Eliminate aeration. In particular, make certain that the brine return discharge line is below the surface in the storage tank during running and that the method of feeding brine from the tank does not cause vortexing with resultant air entrainment. Baudelot type evaporators cause aeration of the chilling liquor and should never be used on brine circuits.
- When cleaning and sterilizing the brine section of a pasteurizer, flush out all brine residues until the rinse water is free of chloride. As an added precaution, it is advisable to form a closed circuit and circulate a 1/4–1/2% caustic soda or sodium metasilicate solution to ensure that any brine residues are rendered alkaline.
- In plate heat exchangers and similar equipment, make sure that stainless-steel brine section components remain free of scale.
- When shutting down the plant after a cleaning run, it is advisable to leave the section full with a dilute (1/4%) caustic solution. Before startup, this should be drained and residues flushed out prior to reintroducing brine.

When operating conditions prevailing in a plant do not permit such a disciplined cleaning, operating, and shutdown procedure, only two materials can be considered for the brine section of a plate heat exchanger. These are Hastelloy C-276 or titanium. The corrosion resistance of both of these materials is such that cleaning and sanitizing of the product side of the heat exchanger can be carried out without removing the brine. Although both are more expensive than stainless steels, especially Hastelloy C-276, the flexibility of plant operation which their use permits could offset their premium price.

Alkaline Detergents

Supplied to food processing plants either as bulk shipments of separate chemicals or as carefully preformulated mixtures, the composition of alkaline detergent formulations can vary widely in accordance with individual preference or the cleaning job to be done. The detergents do, however, generally include some or all of the following compounds:

Sodium hydroxide
Sodium polyphosphate
Sodium metasilicate
Sodium carbonate

Additionally, it is not uncommon to find that a selection of sequestering agents such as EDTA and any of the many available wetting agents also may be present in the formulations.

None of these compounds are corrosive to stainless steels at the concentrations and temperatures used by the food industry for cleaning. Indeed, 316 stainless steel is unaffected by concentrations of sodium hydroxide as high as 20% at temperatures up to 160°C (320°F). They can, therefore, be used with impunity at their usual maximum concentration of 5%, even in ultra-high-temperature (UHT) operation where temperatures can rise to 140°C (284°F).

Companies have reported that some of these preformulated alkaline detergents cause discoloration of the equipment.

The discoloration starts as a golden yellow, darkening to blue through mauve and eventually black. It has been established that this discoloration is caused by the EDTA sequestering agent, which complexes with traces of iron in the water. It then decomposes under certain conditions of pH and temperature to form an extremely fine film of hydrated iron oxide, the coloration being interference colors that darken as the film thickness increases. Although the film is not aesthetically pleasing, it is in no way deleterious and removing it by conventional cleaning agents is virtually impossible.

Some alkaline detergents are compounded with chlorine release agents such as sodium hypochlorite, salts of di- or trichlorocyanuric acid that form a solution containing 200–300 ppm available chlorine at their usage strength. Although the high alkalinity reduces the corrosivity of these additives, generally speaking they should not be employed on a regular basis at temperatures exceeding 70°C (160°F).

Acidic Detergents

Alkaline detergents will not remove the inorganic salts such as milkstone and beer-stone deposits frequently found in pasteurizers. For this, an acidic detergent is required and selection must be made with regard to their interaction with the metal. As was shown earlier, sulfuric and hydrochloric acids will cause general corrosion of stainless steels. Although it could be argued that sulfuric acid can be employed under strictly controlled conditions because stainless steels, especially grade 316, have a very low corrosion rate, its use could result in a deterioration of surface finish. This, in corrosion terms, is an extremely low rate but from an aesthetic viewpoint, is undesirable.

Acids such as phosphoric, nitric, and citric, when used at any concentration likely to be employed in a plant cleaning operation, have no effect on stainless steels and can be used with impunity. Three cautionary notes are worthy of mention:

- It is always preferable to use alkaline cleaning before the acid cycle to minimize the risk of interacting the acid with any chloride salts and, therefore, minimize the formation of hydrochloric acid.
- It is inadvisable to introduce an acid into a UHT sterilizing plant when it is at full operating temperature (140°C/285°F) as part of a "clean-on-the-run" regime.
- Nitric acid, which is a strong oxidizing agent, will attack certain types of rubber used as gaskets and seals. As a general guideline, concentrations should not exceed 1% and temperature 65°C (150°F), although at lower concentrations, the upper recommended temperature is 90°C (195°F).

Another acid that is finding increasing use in the food industry for removing water scale and other acid-soluble scales is sulfamic acid. Freshly prepared solutions of up to 5% concentration are relatively innocuous to stainless steels but problems may arise when CIP systems incorporating recovery of detergents and acids are employed. Sulfamic acid will undergo hydrolysis at elevated temperatures to produce ammonium hydrogen sulfate

$$NH_2SO_2OH + H_2O \rightarrow NH_4HSO_4$$

which behaves in much the same way as sulfuric acid. In situations where the use of this acid is contemplated, prolonged storage of dilute solutions at elevated temperature is inadvisable, although at room temperature the hydrolysis is at a low rate.

Sanitizing Agents

Terminology for the process of killing pathogenic bacteria varies from country to country. In Europe, disinfection is preferred; in America, sanitizing. Regardless, the term should not be confused with sterilization, which is the process of rendering equipment free from all live food spoilage organisms including yeasts, mold, thermophilic bacteria, and most importantly, spores. Sterilization with chemicals is not considered to be feasible and the only recommended procedure involves the circulation of pressurized hot water at a temperature of not less than 140°C (285°F).

For sanitization, while hot water (or steam) is preferred, chemical sanitizers are extensively used. These include noncorrosive compounds such as quaternary ammonium salts, anionic compounds, aldehydes, amphoterics, and potentially corrosive groups of compounds that rely on the release of halogens for their efficacy. By far the most popular sanitizer is sodium hypochlorite (chloros), and this is probably the one material that has caused more corrosion in food plants than any other cleaning agent. For a detailed explanation of the corrosion mechanism, the reader is referred to an article by Boulton and Sorenson (17) that describes a study of the corrosion of 304 and 316 stainless steels by sodium hypochlorite solutions. It is important, therefore, if corrosion is to be avoided, that the conditions under which it is used are strictly controlled. For equipment manufactured from grade 316 stainless steel, the recommended conditions are:

- Maximum concentration—150 ppm available chlorine
- Maximum contact time—20 min
- Maximum temperature—room temperature that is well in excess of the minimum conditions established by Tastayre and Holley to kill *Pseudomonas aeruginosa* (18).

ı addition, several other precautions must be observed:

- Before introducing hypochlorite, equipment should be thoroughly clean and free of scale deposits. Organic residues reduce the bactericidal efficiency of the disinfectant and offer an artificial crevice in which stagnant pools of hypochlorite can accumulate.
- It is imperative that acidic residues be removed by adequate rinsing before introducing hypochlorite solutions. Acid solutions will react with hypochlorite to release elementary chlorine, which is extremely corrosive to all stainless steels.
- The equipment must be cooled to room temperature before introducing hypochlorite. In detergent cleaning runs, equipment temperature is raised to 80–85°C (176–185°F), and unless it is cooled during the rinsing cycle, a substantial increase in temperature of the disinfectant can occur. An important point, frequently overlooked, is that a leaking steam valve can cause a rise in the temperature of equipment even though it theoretically is shut off.
- After sanitizing, the solution should be drained and the system flushed with water of an acceptable bacteriological standard. This normally is done by using a high rinse rate, preferably greater than that used in the processing run.

ıile these comments relate specifically to the sanitizing plate heat exchangers, similar precautions must be en with other creviced equipment. Examples include nually operated valves that should be slackened and plug raised to permit flushing of the seating surface. ıeline gaskets also should be checked frequently to make e that they are in good condition and not excessively dened. Otherwise they will fail to form a crevice-free l over their entire diameter. Where it is not possible to ıpletely remove hypochlorite residues such as in absorbent gland packing materials, hot water is preferred.

All the foregoing relate specifically to sodium hypochlo- solutions but other sanitizing agents that rely on haln release, such as di- and trichlorocyanuric acid, should be used under strictly controlled conditions, including h factors as pH.

odophors also are used for sanitizing equipment. These solutions of iodine in nonionic detergents and contain ıcid such as phosphoric to adjust the pH into the range vhich they exhibit bactericidal efficacy. This group of itizers is employed where hot cleaning is not necessary n lightly soiled surfaces such as milk road tankers, and n tanks. Extreme caution should be exercised with this ıp for, although used at low concentrations (50 ppm), onged contact with stainless steel can cause pitting and crevice corrosion. Furthermore, in storage vessels that have been partially filled with iodophor solutions and allowed to stand overnight, pitting corrosion in the head space has been observed as a result of iodine vaporizing from the solution and condensing as pure crystals on the tank wall above the liquid line. Another factor is that iodine can be absorbed by some rubbers. During subsequent processing operations at elevated temperatures, the iodine is released in the form of organic iodine compounds, especially into fatty foods, which can cause an antiseptic taint. The author knows of one dairy that used an iodophor solution to sanitize a plate pasteurizer to kill an infection of a heat resistant spore-forming organism. The following day, there were over 2000 complaints of tainted milk. CIP cleaning cycles did not remove the antiseptic smell from the rubber seals, and complete replacement with new seals was the only method of resolving the problem.

Another sanitizing agent that is assuming increasing popularity, especially in the brewing industry because of its efficacy against yeasts, is peracetic acid. As such, peracetic acid will not cause corrosion of 304 or 316 stainless steels, and the only precautionary measure to be taken is to use a good quality water containing less than 50 ppm of chloride ions for making up the solutions to their usage concentration. Because of the strongly oxidizing nature of some types of peracetic acid solutions, deterioration of some types of rubber may occur. A recent survey undertaken by the IDF for the use of peracetic acid in the dairy industry (19) found few corrosion problems reported. The general consensus of opinion was that it permitted greater flexibility in the conditions of use, compared with sodium hypochlorite, without running the risk of damage to equipment.

For comprehensive information on the cleaning of food processing equipment, albeit primarily written for the dairy industry, the reader is referred to the British Standards Institute publication BS 5305 (20).

CORROSION BY INSULATING MATERIALS

Energy conservation now is widely practiced by all branches of industry, and the food industry is no exception. For example, in the brewing industry, wort from the wort boilers is cooled to fermentation temperature, and the hot water generated in the process is stored in insulated vessels (hot-liquor tanks) for making up the next batch of wort. An area of corrosion science that is receiving increased attention is the subject of corrosion initiated in stainless steels by insulating materials. At temperatures in excess of 60°C (140°F) these can act as a source of chlorides that will induce stress corrosion cracking and pitting corrosion of austenitic stainless steels.

Among the insulating materials that have been used for tanks and pipework are

Foamed plastics—polyurethane, polyisocyanurate, phenolic resins, etc
Cellular and foamed glass
Mineral fiber—glass wool, rock wool
Calcium silicate

Magnesia
Cork

All insulating materials contain chlorides to a lesser (10 ppm) or greater (1.5%) extent. The mineral based insulants such as asbestos may contain them as naturally occurring water soluble salts such as sodium or calcium chloride. The organic foams, on the other hand, may contain hydrolysable organochlorine materials used as blowing agents (to form the foam), fire retardants such as chlorinated organophosphates, or chlorine containing materials present as impurities. Insulation manufacturers are becoming increasingly aware of the potential risk of chlorides in contact with stainless steels and are making serious efforts to market a range of materials that are essentially chloride-free.

A point not frequently appreciated is that even though many of the insulating materials contain high levels of chloride, in isolation they are not corrosive.

Corrosion, which is an electrochemical process, involves ionic species, and in the absence of a solvent (water) the chloride or salts present in the insulation cannot undergo ionization to give chloride ions. Therefore, they are essentially noncorrosive. Similarly, where organochlorine compounds are present, water is necessary for hydrolysis to occur with the formation of hydrochloric acid or other ionisable chloride compounds.

The main problem, therefore, is not so much the insulant but the interaction of the insulant with potential contaminants to release corrosive species. Under ideal conditions, that is, if the insulating material could be maintained perfectly dry, the chloride content would not be a critical factor in the material specification process. Unfortunately, it must be acknowledged that even in the best regulated installation, this ideal is rarely (if ever) achieved and therefore, thought must be given to recommended guidelines.

Any material that is capable of absorbing water must be regarded as a potential source of chloride. Although the chloride content of the insulant may be extremely low (25 ppm), under extractive conditions when the insulation becomes wet and concentration effects come into play, even this material may cause the initiation of stress corrosion cracking. The chloride content of the contaminating water cannot be ignored. Even a "good-quality" water with a low chloride content (30 ppm), if being continuously absorbed by the insulant, forms a potential source of chlorides that, through evaporation, can reach very significant levels and initiate the corrosion mechanism.

The more absorptive the insulant, the greater the risk, and materials such as calcium silicate and certain types of foams must be regarded as least desirable. It is interesting to note that one of the least absorptive insulants from those listed is cork, and in the experience of the author, there have been no reported cases of this insulant causing problems with stress corrosion cracking of stainless steels. Of course, it could be argued that the bitumen used as an adhesive to stick the cork to the vessel walls has to be applied so thickly that the bitumen forms an impermeable barrier preventing contact of the contaminated water with the stainless-steel substrate. Irrespective of the protection mechanism, the net effect is that cork has an extreme good "track record." Unfortunately, due to the cost, cork now rarely used.

No hard-and-fast rules can be laid down for specifyi the acceptable maximum tolerable chloride content of insulating material. Any specification must take into count what is commercially available as well as all t other factors such as price, flammability, and ease of a plication. To specify zero chloride is obviously impractic and even a figure of 10 ppm may be difficult to achieve commercially available products. As a general comp mise, 25 ppm maximum is considered to be technically a commercially feasible while minimizing the potenti source level of chloride corrodent.

The primary function of the insulant is to provide thermal barrier between the outside of the vessel and t environment. It does not provide a vapor or moisture ba rier, and provision of such protection must be regarded equally important in the insulating process. As mention previously, the use of bitumen as an adhesive for cork i sulation must provide an extremely good water barrier, though there are a wide range of products marketed sp cifically for this purpose. These include specially develop paints of undefined composition and zinc free silico alkyd paints as well as silicone lacquer. These silico based products are particularly appropriate because their inherent low water permeability and also their st bility at elevated temperatures. Aluminum foil has al been successfully used as a water-vapor barrier betwe the stainless steel and the insulant. There is little dou that the foil provides an extremely good barrier but at la between the sheets of foil, ingression of water can occ unless sealing is complete, the achievement of which most unlikely. Furthermore, it is likely that there will tears in the foil, providing yet another ingression path f water. However, it is believed that aluminum foil has a ro additional to that of a barrier. As it is, from an electr chemical aspect, "anodic" to stainless steel, it will provi galvanic protection of the steel in areas where there is "holiday" in the foil, thus inhibiting corrosion mechanism

When insulation material becomes wet, the insulati efficiency shows a dramatic fall-off. In fact, the therm conductivity of wet insulation will approach that of t wetting medium, and it is ironic that the thermal cond tivity of water is among the highest known for liquids is imperative that from the standpoint of preventing mo ture ingression to minimize corrosion risks and main insulation efficiency, the insulation is externally prote from rain and water. There is a variety of materials ava able for this such as aluminum sheeting, plastic-coat mild steel, and spray applied polyurethane coatings. Mu of the value of the protection will be lost unless particu attention is taken to maintaining a weather-tight seal the overlaps in individuals sheets of cladding. There a many semiflexible caulking agents that can be employe for this. One that is particularly effective is the RTV silico rubber, which exhibits extremely good weather resistan and long-term reliability. Nevertheless, maintenance is quired, especially around areas of discontinuity such flanged connections and manway doors. Operators are b ginning to realize that routine maintenance work on

Table 5. Some Synthetic Rubbers

Rubber	Common trade names	Basic structure
Polychloroprene	Neoprene Perbunan C Butachlor Nairit	Poly (2-chlor-1,8 butadiene)
SBR (styrene butadiene rubber)	Buna S Plioflex Intol Krylene	Copolymer of styrene and 1,4 butadiene
Nitrile	Buna N Chemigum N Paracril Perbunan Hycar	Copolymer of acrylonitrile and 1,4 butadiene
EPDM (ethylene propylene diene methylene)	Nordel Royalene Vistalon Dutral Keltan Intolan	Copolymer of ethylene and propylene with a third monomer such as ethylidene norbonene, cyclopentadiene
Butyl	GR-1 Bucar Socabutyl	Copolymer of isobutylene and isoprene
Silicone	Silastic Silastomer Sil-O-Flex	Poly(dimethyl siloxane), poly(methyl vinyl siloxane), etc.
Fluoroelastomer	Viton Technoflon Fluorel	Copolymer of hexafluoropropylene and vinylidene fluoride

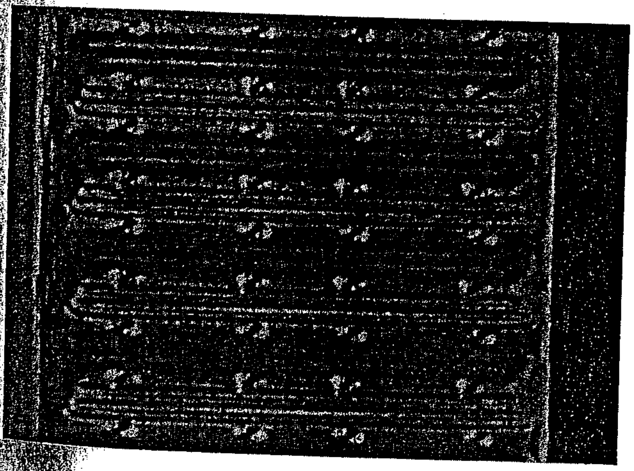

Figure 23. Catastrophic failure of the gasket groove of a heat-exchanger plate by stress corrosion cracking caused by the use of a polychloroprene based adhesive.

sulation is as important as that on all other items of plant and equipment.

It will be appreciated from all the foregoing that insulation of a vessel or pipeline is a composite activity with many interactive parameters. It is impossible to lay down specification rules, as each case much be viewed in the light of requirements. These notes must, therefore, be regarded as guidelines rather than dogma, and for further information, an excellent publication by the American Society for Testing Materials (21) is essential reading.

CORROSION OF RUBBERS

Many involved in the field of corrosion would not regard the deterioration of rubber as a corrosion process. The author's opinion differs from this viewpoint as "rubber undergoes deterioration by interaction with its environment."

General

Rubber and rubber components form an essential part of food processing equipment—joint rings on pipelines, gaskets on heat exchangers, and plate evaporators. Although natural rubber was the first material to be used for manufacturing these components, nowadays they are made almost exclusively from one of the synthetic rubbers listed in Table 5.

Unlike metals and alloys, which have a strictly defined composition, the constituents used in the formulation of rubbers are rarely stipulated. More often, they will reflect the views and idiosyncrasies of the formulator on how to achieve the desired end product. The important constituents of a rubber are

- *Basic Polymer*. Largely determines the general chemical properties of the finished product.
- *Reinforcing Fillers*. These are added to improve the mechanical properties and will invariably be one of the grades of carbon black—or if a white rubber is required, mineral fillers such as clays or calcium silicate.
- *Vulcanizing Agents*. These cross-link the basic polymer and impart rubberlike properties that are maintained at elevated temperatures.
- *Antioxidants*. To stabilize the rubber against oxidative degradation, hardening or softening, after prolonged operating periods at elevated temperatures.
- *Processing Aids*. Which facilitate the molding of the rubber.
- *Plasticizers*. To modify the mechanical properties.

A complicating factor to be considered when formulating rubber for food-contact surfaces is the acceptability (or nonacceptability) of the compounding ingredients. Some countries, notably Germany and the USA, have drawn up lists of permitted ingredients (22,23), while other countries regulate the amount of material that can be extracted from the finished article by various test media.

Invoking these regulations may impose limits on the in-service performance of a rubber component, which could be a compromise, exhibiting desirable properties inferior to those achievable were it for a nonfood application. For example, the resistance to high pressure steam of some rubbers can be enhanced by using lead oxide as an ingredient. Obviously, such materials could not be contemplated for any food contact application.

Table 6. Performance of Rubbers in Some Environments Found in the Food and Beverage Industries

	SBR	Medium nitrile	Natural rubber	Polychloroprene	Butyl	EPDM	Sili
			Products				
Whole milk	E	E	E	E	E	E	
Beer, wines, spirits	G-F	E	F	E	E	E	
Fats, oils, cream	F	E	F	G	P	G	
Sauces	E	E	F[b]	E	E[b]	E	
Salad dressings	F	E	F	G	P	G	
Fruit drinks and juices[d]	E	E	G	E	E	E	
			Cleaning Agents				
Sodium hydroxide[c]	G	E	G	G	E	E	
Sodium carbonate[f]	E	E	E	E	E	E	
Sodium hypochlorite[g]	G	G	G	G	E	E	
Nitric acid[h]	F	F	P	F	G	G	
Phosphoric acid[i]	E	E	E	E	E	E	
Quaternary ammonium compounds[e]	E	E	E	E	G	G	

[a] Depending on the type of basic polymer.
[b] Depending on the fat/oil content.
[c] Used as an aqueous 1% solution.
[d] The performance of a rubber will be affected by the presence of essential oils.
[e] All strengths up to 5% at maximum operating temperatures of the rubber.
[f] Sodium carbonate and other detergent/additives, eg, sodium phosphate, silicate.
[g] Sodium hypochlorite as used at normal sterilizing concentration—150 mg/L.
[h] Nitric acid as used at normal cleaning strength of 1/2-1%.
[i] Up to 5% strength.

Table 7. Suggested Limits of Concentration and Temperature for Peracetic Acid in Contact with Rubber

Peracetic acid concentration (active ingredient)	Temp. (°C)	Medium nitrile	Butyl (resin-cured)	EPDM	Silicon	Fluoro-elas
0.05% (500 mg/L)	20	R[a]	R	R	R	R
	60	R	R	R	R	R
	85	(?)	R	R	R	(?)[b]
0.10% (1 g/L)	20	R	R	R	R	R
	60	NR[c]	R	R	NR	R
	85	NR	(?)	R	NR	NR
0.25% (2.5 g/L)	20	R	R	R	(?)	R
	60	NR	R	R	NR	R
	85	NR	NR	R	NR	NR
0.5% (5 g/L)	20		R	R	NR	R
	60	NR	R	R	NR	R
	85	NR	NR	R	NR	NR

[a] R—Little effect on the rubber.
[b] (?)—Possibly some degradation.
[c] NR—Not recommended as significant degradation may occur.

Corrosion by Rubber

The majority of rubbers and formulating ingredients have no effect on stainless steels even under conditions of high temperature and moisture. There are two notable exceptions, namely, polychloroprene and chlorosulfonated polyethylene. Both of these contain chlorine, which under the influence of temperature and moisture, undergo hydrolysis to produce small quantities of hydrochloric acid. In contact with stainless steel, this represents a serious corrosion hazard causing the three main forms of attack.

When specifying a rubber component, it is easy to avoid these two polymers but a fact not often appreciated is that many of the rubber adhesives are produced from
these polymers. That is the reason why manufactu
heat exchangers and other equipment, which neces
sticking the rubber onto metal, specify what type
hesive should be used. Many DIY adhesives and
adhesives are formulated from polychloroprene, a
not unknown for a maintenance engineer having
gaskets in a heat exchanger to get the supply of
cement from the local hardware shop. The results
catastrophic, as shown in Figure 23. Similarly, m
adhesive tapes used as a polychloroprene-based a
and direct contact of these with stainless steels sh
avoided.

Corrosion of Rubber by Environments

From the standpoint of food processing, the environments likely to interact with rubber are classified under the following headings:

- Foodstuffs containing no fat or a low level of fat, eg, milk
- Fatty products: butter, cream, cooking oils, shortenings
- Alkaline detergents
- Acid detergents
- Sanitizing agents

Unlike the corrosion of metals, which is associated with oxidation and loss of metal, rubber deterioration usually takes other forms. When a rubber is immersed in a liquid, it absorbs that liquid or substances present in it to a greater or lesser degree. The amount of absorption determines whether the rubber is compatible with the environment. The absorption will be accompanied by changes in mass, volume, hardness, and tensile strength. For example, immersing and oil resistant rubber in vegetable oil may produce a change in volume of only 2–3%, whereas a non-oil-resistant rubber may swell by 150% or more. Such a volumetric change will be accompanied by a large reduction in the tensile strength and a high degree of softening.

Broadly, speaking, a rubber should not exhibit a volumetric or weight change greater than 10% nor a hardness change of more than 10 degrees (International Rubber Hardness Degrees—IRHD or Shore A) to be classed as compatible. For general guidance, data presented in Tables 6 and 7 (19) indicate the compatibility of rubbers with some food industry environments. But for more information, the reader should refer to one of the national or international test procedures (24–26).

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CRABS AND CRAB PROCESSING

Crabs play an important part in the U.S. fishing industry. Ex-vessel landings and values usually rank low in quantity (Fig. 1) and high in value (Fig. 2). The quantity and value of the major crab fishes in the United States in 1996 are shown in Table 1 (1). Variations in processing methods for crabs are related to the species and the seasonal characteristics that affect yield, ease of meat removal, and color. Speed in handling the product from time of harvesting to freezing or canning is a most important process requirement (2,3). Quality control procedures generally emphasize sanitation, food regulatory requirements, and compliance with end-product specifications of the processor (4).

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CORROSION INHIBITORS

Eldredge and Warner (1) state "any substance which when added in small amounts to the corrosive environment of a metal or an alloy effectively decreases the corrosion rate, is called an inhibitor." The concept has long been known, as in the use of natural products such as gelatin and glue as inhibitors for the corrosion of iron in pickling acids (2), tannin (3) for prevention of boiler corrosion, and bone oil in producing oil and gas wells. The number of materials—either natural products, proprietary compounds, or individual chemical species—used as inhibitors is legion and published references on the subject in technical and trade journals and patent literature are too voluminous to be covered in any detail in an article of this length. This situation is not surprising when one considers that corrosion in both its technical and economic importance is one of the most serious problems in chemical technology.

Estimates of costs due to both direct and indirect corrosion losses in American industry vary between 5 and 10 billion dollars annually. The accelerating technological developments of the past twenty years have resulted in equipment being operated at increasingly higher temperatures, flow rates, and pressures, and under increasingly severe chemical environments. Meanwhile, continuing demands have been made for improved product purity and system reliability. At the same time, costs of materials and labor have risen disproportionately to product selling costs. It is therefore not surprising that intensive efforts have been carried out in commercial, governmental, and university research and engineering groups to reduce and control corrosion. The importance of corrosion control may be expected to continue, and even to increase, as our technical progress accelerates in the future.

Corrosion inhibitors offer only one method of corrosion control. They may be replaced or augmented by other methods such as construction materials selection, protective coatings, and cathodic as well as anodic protection—depending on the technical and economic aspects of the specific corrosive situation. Nevertheless, their use is widespread, and the control of corrosion by inhibitors has itself given rise to a sizeable industry. Original references to corrosion inhibitors in published literature are so very numerous that it is a considerable effort even to a worker in this specific field to keep up with them. Fortunately, there are several excellent secondary sources which have already been compiled in the literature, and it is suggested that the reader who is interested in further knowledge of corrosion inhibitors consult these secondary sources as his next step in developing information in this field. This article will refer, whenever possible, to the secondary sources in which the primary sources are not only listed, but collated with other references and critically evaluated.

Types of Inhibitors

Passivators. Some inhibitors, but by no means all, act as passivators. The preceding article, Corrosion, summarizes current views: "Passivators may be regarded as corrosion inhibitors which result in the inhibited metal assuming the potential and electrochemical behavior of a noble metal." Further, "considerable progress has been made in understanding the functioning of passivators, but not to the extent that controversy fails to exist" and "many inhibitors are not in themselves passivators, but cooperate with oxygen or other oxidizing agents (including anodic current) to produce the passive state." Electrochemical studies using potentiostatic or galvanostatic equipment are used extensively in investigating passivity. Essentially, by reaction with organic matter, etc, to Cr^{3+} which is not an inhibitor. Hence, green color indicates decreased CrO_4^{2-} concentration and is a danger signal. When the color changes from yellow to green, fluids should be flushed out and changed with replenished chromate inhibitor at the recommended concentration. This varies from several hundred ppm for freshwaters to as high as 0.5–1% for high-chloride brines.

Some mixtures of anodic inhibitors are less susceptible to the pitting type of attack at low concentrations than are their individual constituents. Thus, the "dianodic process" containing mixtures of chromate and condensed phosphate is purported to avoid this type of attack (9,10). Wormwell (10) and co-workers at the National Physical Laboratory in England have reported on the use of sodium benzoate at pH $\geq$ 6 and in concentrations of 1% for inhibition of chloride-containing waters

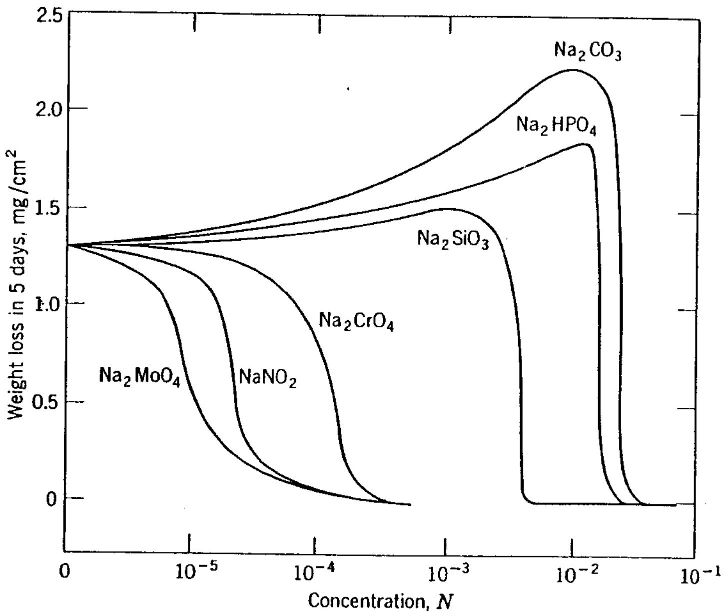

Fig. 1. Effect of concentration of various inhibitors on the corrosion of iron (7a). Courtesy *Journal of the Electrochemical Society.*

There is no acceleration of intensity of attack with these materials, although the high inhibitor concentration precludes its use in many systems. Cartledge (11) has described the effectiveness of the pertechnetate ion (as $KTcO_4$) which gives outstanding inhibitor effectiveness even at 5–10 ppm, a very low concentration for an inorganic ion. This material, a by-product of the nuclear reactor at Oak Ridge, Tennessee, is not available commercially.

In the discussion of passivating inhibitors in water systems, the following factors must be considered: (*1*) These inhibitors are often dangerous in low concentrations. (*2*) Required concentrations vary greatly, depending upon the system. (*3*) In circulating systems, the inhibitor costs may be allowable; whereas in once-through systems, they are not. (*4*) Effectiveness of inhibitors is often greatly dependent on oxygen access to the metal surface. This, in turn, depends on the amount of oxygen dissolved in the system, the circulation rate or fluid velocity, temperature, salinity, and

United States Patent [19]

May

[11] **Patent Number: 4,851,130**

[45] **Date of Patent: Jul. 25, 1989**

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[54] **OXYGEN REMOVAL WITH CARBON CATALYZED ERYTHORBATE OR ASCORBATE**

[75] Inventor: **Ralph D. May**, Oakdale, Conn.

[73] Assignee: **Pfizer Inc.**, New York, N.Y.

[21] Appl. No.: **278,127**

[22] Filed: **Nov. 30, 1988**

[51] **Int. Cl.⁴** **C02F 1/20**; C23F 11/10

[52] **U.S. Cl.** **210/750**; 210/757; 210/766; 422/17; 252/178

[58] **Field of Search** 210/668, 669, 694, 750, 210/757, 763, 765, 766; 422/13, 14, 16, 17; 252/178, 390–404

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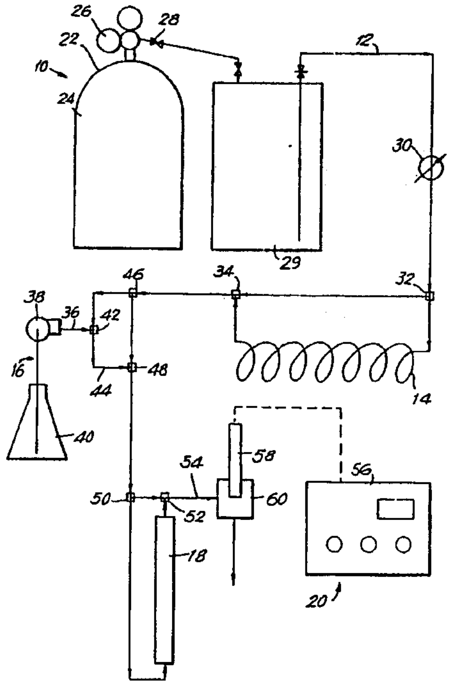
Primary Examiner—Tom Wyse

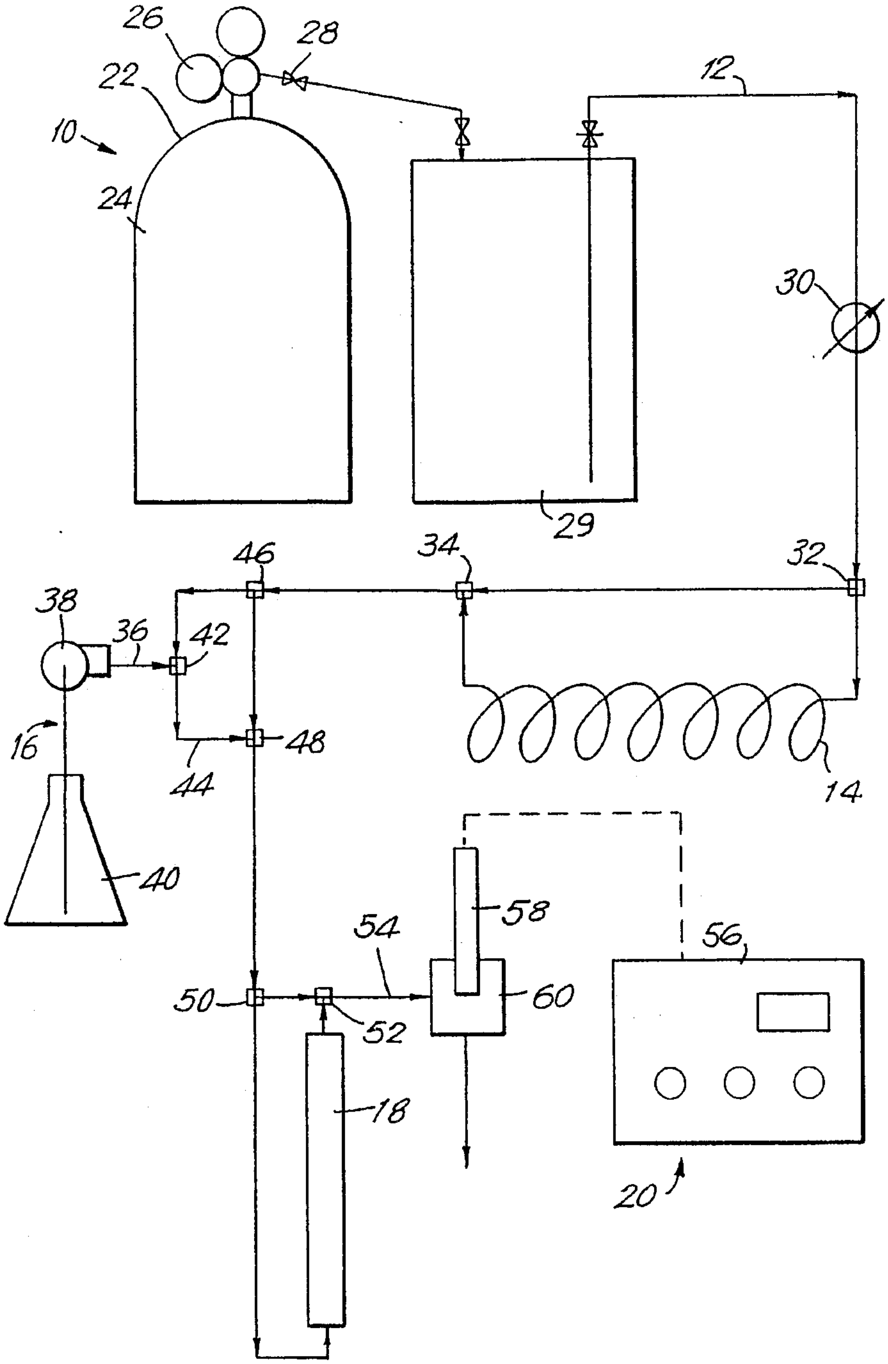
Attorney, Agent, or Firm—Peter C. Richardson; Paul H. Ginsburg; Gezina Holtrust

[57] **ABSTRACT**

When an aqueous system containing dissolved oxygen and erythorbate or ascorbate is passed through an activated carbon bed, the oxygen is removed at ambient temperatures. This method of oxygen removal finds practical application in the removal of oxygen from boiler condensate, low temperature boiler feedwater and oil well injection water or brine.

10 Claims, 1 Drawing Sheet

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OXYGEN REMOVAL WITH CARBON CATALYZED ERYTHORBATE OR ASCORBATE

BACKGROUND OF THE INVENTION

This invention relates to the removal of oxygen from aqueous system such as boiler feedwater and oil well injection water. Such oxygen removal is achieved with erythorbic acid, erythorbate, ascorbic acid, or ascorbate, with the aid of activated carbon.

The use of erythorbic acid as an oxygen remover or scavenger in boiler feedwater is described in Kelly et al U.S. Pat. No. 4,419,327. At the high temperatures and pressures of the boiler system, erythorbic acid is capable of reacting with oxygen very rapidly in the absence of activated carbon. At ambient temperature, however, erythorbic acid reacts too slowly to be of practical value.

Meyers et al U.S. Pat. No. 4,627,921 discloses deoxygenation of water at ambient temperature by passing the water with a reducing agent such as hydrazine, morpholine, sodium sulfite, and sodium acid sulfite through an adsorbent, absorbent bed which may be made of activated carbon. The present invention introduces further oxygen scavengers having advantages not attained with the above four reducing agents of Meyers et al.

SUMMARY OF THE INVENTION

According to the invention, dissolved oxygen is removed from an aqueous system by contacting said aqueous oxygen-containing system with an oxygen scavenger selected from the group consisting of erythorbic acid, erythorbate, ascorbic acid, and ascorbate, and with activated carbon.

The oxygen-containing system may be contacted with the oxygen-scavenger in the presence of the activated carbon on the system may be contacted with the oxygen-scavenger before contact with the activated carbon. Preferably, the oxygen-containing system is first contacted with a solution of the oxygen scavenger before contacting with the activated carbon.

Generally, the pH of the aqueous system ranges from about 5 to about 9.5. Examples of aqueous systems from which dissolved oxygen may be removed are oil well injection brine, oil well injection water, boiler condensate, and low temperature boiler feedwater.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE of the drawing shows an apparatus for testing carbon catalyzed oxygen scavinging.

DETAILED DESCRIPTION OF THE INVENTION

The amount of oxygen scavenger needed for oxygen removal from an aqueous system depends on parameters such as the amount of oxygen present in the aqueous system, and the type of scavenger used. In general, the amount of oxygen scavenger ranges from about 10 to 15 parts per part of oxygen in the system.

The present oxygen scavengers are effective in aqueous systems having ambient or slightly lower than ambient temperatures, e.g. about 39° F. (4° C.) to 149° F. (65° C.), and higher. Ambient temperature is understood to be the temperature at the reaction site. The present method is therefore useful in boiler feedwater usually having low temperatures of at most 180° F. (82° C.), usually at most 150° F. (66° C.), and in oil well injection water or brine having ambient temperatures.

The present method is effective at the usual pH of about 8 to 9.5 of boiler feedwater, and the usual pH of about 5 to 9.5 of oil well injection water. Thus, the pH conditions may vary from about slightly acidic to slightly alkaline. In comparison, the sulfite currently used in boiler feedwater and oil well injection brine or water requires a pH of about 7 to 8 for effective oxygen removal.

Preferably, the oxygen scavenger is a soluble salt of erythorbic acid such as ammonium, sodium, potassium, calcium or zinc erythorbate. Sodium erythorbate monohydrate is particularly suitable since it is commercially available. A soluble salt of ascorbic acid is less preferred because of the higher cost thereof.

The present oxygen scavengers are effective at the high temperatures of oil field applications and boiler systems. In comparison, sulfite can not be used in systems that operate under pressures of higher than about 1,000 psi.

The activated carbon of use in the present method is capable of promoting the reaction of oxygen with one of the oxygen scavengers of the invention at the above mentioned relatively low temperatures. The activated carbon is in general a carbon having a large surface area. The efficiency of the active carbon decreases with increasing size of the carbon particles, so longer residence times are required with beds of larger particle sizes, and shorter residence times with beds of smaller particle sizes. Larger carbon particles of e.g. about 5 mm, form less efficient scavengers because of the smaller total surface available for catalyzing the reaction. However, the particle size should not be so small, e.g. about 100 mesh, as to cause washing away of the particles during use. Advantageously, the

The following Examples illustrate the invention. The temperatures are in degrees Celsius.

EXAMPLES 1-5

The drawing shows an experimental apparatus used to simulate the conditions of the aqueous systems, oxygen concentration etc. in practical application of the invention. System **10** comprising six components: a gas regulator **11**, a reservoir and delivery system for water **12**, a cooling coil **14**, a delivery system for erythorbate **16**, a carbon bed **18**, and an oxygen analyzer **20**.

The gas regulator **22** consists of a cylinder of compressed helium **24**, a pressure regulator **26**, and an on/-off valve **28**.

The reservoir and delivery system **12** consists of a tank **29**. The tank is pressurized with compressed helium at 10 p.s.i.g. to drive the water contained in the tanks through the treatment system **10**. The flow rate of the water if regulated by a metering valve **30**.

The cooling coil **14** is contained in a plastic pail (not shown) which is filled with ice and water. Most experiments do not require cooling and the cooling coil is then bypassed using three-way valves **32** and **34**.

The erythorbate solution is fed through outlet **36** using a metering pump **38**. The erythorbate solution is formed by dissolving sodium erythorbate in deoxygenated water in an erlenmeyer flask **40** and the solution is protected by a nitrogen blanket. The solution is pumped to a mixing tee **42** in injection loop **44**. When the solution is not fed into the system, the injection loop **44** is bypassed by using three-way valves **46** and **48**.

The carbon bed **18** consists of a cylinder of packed active carbon. The aqueous system exiting from three-way valve **48** flows upward through the carbon bed facilitating flushing of gas bubbles from the aqueous system. The carbon bed **18** may be bypassed using three-way valves **50** and **52**.

The oxygen content of the aqueous system in line **54** is measured by the oxygen analyzer **20** (Orbisphere model 2713) consisting of a meter **56**, a probe **58**, and a flow cell **60**. The analyzer **20** can measure 0.1 ppb dissolved oxygen at temperatures of 0 to 45° C. and flow rates of 50 to 250 ml/min.

TABLE

	Sodium Erythorbate Concentration	Oxygen Concentration		Reaction Time*	Temperature	Carbon Bed Dimensions (diameter by length)	Carbon Type	Aqueous System	Flow Rate
		initial	final						
EXAMPLE 1	162 ppm	8.9 ppm	0.4 ppm	6 min.	20° C.	4" × 15"	Darco 12 × 20	water	450 ml/min
EXAMPLE 1A	162 ppm	12 ppm	10.7 ppm	6 min.	20° C.	no carbon		water	450 ml/min
EXAMPLE 1B	0	12 ppm	11.9 ppm	6 min.	20° C.	4" × 15"	Darco 12 × 20	water	450 ml/min
EXAMPLE 2	162 ppm	12 ppm	1.2 ppb	2.25 min	21° C.	2" × 12"	Darco 12 × 20	brine	200 ml/min
EXAMPLE 3	108 ppm	8 ppm	1-2 ppb	50 sec	21° C.	2" × 4"	Darco 20 × 40	water	200 ml/min
EXAMPLE 4	9.1 ppm	675 ppb	1.2 ppb	2.25 min	4° C.	2" × 12"	Darco 12 × 20	brine	200 ml/min

*The reaction time is the liquid volume of the carbon bed divided by the flow rate.

The Table sets forth the results of five experiments with oxygen scavinging of water or brine. The brine solution is a synthetic North Sea brine solution prepared from the following:

24.8 g calcium chloride
215.2 g magnesium chloride hexahydrate
85.8 g sodium sulfate
4.2 g sodium bicarbonate
476.8 g sodium chloride

The above was dissolved in water to make 20 liters. The amount of oxygen present in the aqueous systems in the tank varies depending on whether tap water is used having a relatively high oxygen concentration of about 8-12 parts per million (ppm) or oxygenated boiler condensate having lower oxygen concentrations of 675 and 713 parts per billion (ppb).

The particle size specifications of the activated carbon are as follows:

Comparative Example 1A shows the effect of omitting the active carbon bed of Example 1 on the amount of oxygen scavenged. Comparative Example 1B shows the effect of omitting the sodium erythorbate of Example 1. The remaining Examples show the use of both the oxygen scavenger and the active carbon bed under different reaction conditions. Example 2 shows scavenging of a brine at a relatively short reaction time. Example 3 shows scavenging with a carbon bed of relatively small particle size and relatively small bed size. Example 4 shows scavenging of a brine having a low initial oxygen concentration at a low temperature.

I claim:

1. A method of removing dissolved oxygen from an aqueous system comprising contacting said aqueous oxygen-containing system with an oxygen scavenger selected from the group consisting of erythorbic acid, erythorbate, ascorbic acid, ascorbate, and with activated carbon.

2. A method according to claim 1 wherein said contacting with said oxygen scavenger is in the presence of said activated carbon.

3. A method according to claim 1 wherein said contacting with said activated carbon is after said contacting with said oxygen-scavenger.

4. A method according to claim 1 wherein said aqueous system is an oil well injection water or oil well injection brine.

5. A method according to claim 1 wherein said aqueous system has a pH of about 5 to about 9.5.

6. A method according to claim 1 wherein said aque-

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CORROSION AND CORROSION INHIBITORS

Corrosion is defined as the destructive attack of a metal by the environment, by chemical or electrochemical processes. Corrosion does not include the wasting of a metal by mechanical means such as the erosion of a metal structure by sand in the desert; but it does include conjoint mechanical and chemical action to produce early failure of a load-carrying metal structure. Stress-corrosion cracking, for example, is produced by the conjoint action of mechanical stress and specific chemical agents. The usual connotation of corrosion is one of an undesirable phenomenon; however, in technology there are many cases of useful corrosion. Among these are the formation of decorative coatings on metal items and the controlled corrosion of zinc in a primary cell to produce electrical energy (see Batteries).

In this article corrosion is treated as an undesirable wastage of metal and metal structures and consideration is given to its prevention.

Manifestations of Corrosion

The most common form in which corrosion appears is uniform attack. The entire metal surface is covered with the corrosion product. The rusting of iron in any humid atmosphere and the tarnishing of copper and silver alloys in sulfur-containing environments are examples. High temperature oxidation, or dry oxidation, is usually uniform in character.

An especially pernicious type of attack is called pitting corrosion. In such cases a pit or a number of pits may cause considerable damage to a metal structure, or may indeed penetrate the structure without the metal exhibiting any appreciable loss in weight. Pitting corrosion is usually seen on metals that are normally passivated with an oxide film. Aluminum alloys, such as those used in household storm window frames, exhibit this type of attack. Stainless steels of the nickel–chromium type exposed to quiet seawater will pit.

Several of the conjoint types of corrosion attack appear as cracking failures. In stress-corrosion cracking a metal part exposed simultaneously to a constant tensile stress and a specific corroding agent will crack intergranularly (between the metal grains) or transgranularly (across the metal grains). When the stress is cyclic rather than constant the failure is termed corrosion fatigue. Stress-corrosion cracking has assumed such importance in modern technology that this subject is discussed in more detail below.

Corrosion may appear in the form of intergranular attack. Often intergranular attack is the result of stress corrosion, but can also occur because the grain boundary and grain proper have different tendencies to corrode, ie, different electrical potentials. Intergranular attack becomes serious because it results in a loss in strength or ductility of the metal.

A further type of attack has been described as dezincification. Certain alloys of importance in commerce such as the Cu–Zn alloys contain a reactive metal (Zn) and a more noble metal (Cu). Upon exposure to a particularly corrosive environment the brass becomes covered with a reddish film suggesting that the zinc has gone into the solution and the copper remained behind. Actually, both elements dissolve and the copper is redeposited to form the reddish appearing surface.

Copper–aluminum alloys are also subjected to the same type of attack as are gold–silver alloys. In the latter case the reaction has been called parting.

Most of the observed corrosion occurs as one or more of these five cases. There are some special forms of corrosion such as the dissolution of a metal or alloy in a hot fused salt bath which are difficult to categorize.

Origin of Corrosion

The most common origin of corrosion is the basic thermodynamic tendency for metal to react as expressed in terms of the free energy of reaction (see Thermodynamics). However, in most cases of interest in engineering there are factors imposed on this basic tendency that accelerate the corrosion rate.

Some free energies of formation of compounds important in corrosion are given in Table 1 (1). The free energy of formation of the compound is the free energy for the reaction of the elemental metal with the other chemical species also in its elemental state, eg,

$$2\,\mathrm{Fe} + \frac{3}{2}\mathrm{O_2} \rightarrow \mathrm{Fe_2O_3} \quad \Delta G^\circ = -741.0\ \mathrm{kJ/mol}\ (-177.1\ \mathrm{kcal/mol})$$

The negative free energy of formation indicates a tendency for the metal to react, that is, the oxide is stable. A positive ΔG° indicates that the elemental metal is stable; note the positive ΔG° for Au_2O_3 (Table 1).

Although a large free energy of formation indicates that the formation of the compound is favored thermodynamically, the specific reaction may not go readily because of a high activation energy for the reaction. This is illustrated by the corrosion of lithium metal by air and its component gases. A comparison of free energy of formations of compounds that should be obtained from the exposure of the metal to several gases in air indicates that lithium should react readily with dry oxygen and dry carbon dioxide to form Li_2O and Li_2CO_3. However, a detailed study of the reactivity of Li metal with gases (2) showed that there was no detectable reaction with Li under 250°C. Water vapor is required for the reaction of Li with CO_2, probably as:

Cadmium plating is a useful cathodic protection measure that does not risk over-protection, but hydrogen either must not be codeposited with cadmium to a dangerous degree, or if codeposited (as is the case with the cyanide plating bath), it must be safely redistributed by thermal treatment before the high-strength steel component is stressed; otherwise the steel may experience hydrogen-embrittlement cracking which can be as serious a problem as SCC, if not worse.

Stainless Steels. Austenitic stainless steels undergo SCC when stressed in hot aqueous environments containing chloride ion. The oxygen level of the environment can be important, probably through its effect in establishing the electrode potential of the steel. The total matrix of combinations of stress level, chloride ion and oxygen concentrations, and temperature that will cause SCC has not been worked out. At about yield strength stress and about 290°C, 1 ppm Cl^- and 1 ppm O_2 are approximately the minimum levels that initiate SCC. At room temperature, chloride SCC seldom occurs in austenitic stainless steels except when they are heavily sensitized. If they are not heavily sensitized, there is not usually a problem except at elevated temperatures. There is no well defined threshold temperature for vulnerability to SCC in stainless steels, but above about 60°C it becomes of increasing concern.

The relative susceptibilities of the common grades of austenitic stainless steel to chloride SCC do not differ greatly, although the steels that can and do become sensitized are decidedly inferior in this condition. The high purity ferritic grades of stainless steel, which have become commercially available only recently, offer appreciable improvement in SCC resistance compared with the austenitic grades, but they are not immune to cracking; care must also be exercised to avoid the ductile-to-brittle transition problem and the potential embrittlement by sigma-phase formation in elevated temperature service. The standard methods for avoiding chloride SCC in austenitic stainless steels include avoiding introducing fabrication stresses, minimizing chloride ion level, and minimizing oxygen concentration in the environment. Additionally, where feasible, it is possible to mitigate against SCC in these alloys by cathodic protection, such as can be provided by coupling to iron or to lead.

Corrosion Resistant Materials

A large number of alloys has been developed with varying degrees of corrosion resistance in response to various environmental needs. At the lower end of the alloying scale are the low alloy steels. These are iron-base alloys containing from 0.5–3.0% of Ni, Cr, Mo, or Cu and controlled amounts of P, N, and S with the exact composition varying with the manufacturer. The corrosion resistance of the alloy is based on the protective nature of the surface film, which in turn is based on the physical and chemical properties of the oxide film. As a rule, this alloying will reduce the rate of rusting by 50% over the first few years of atmosphere exposure. These low alloy steels have been used outdoors without protection.

The stainless steels contain appreciable Cr, Ni, or both. The straight chrome steels, types 410, 416, and 430, contain about 12, 13, and 16% Cr, respectively. The chrome–nickel steels include type 302 (18% Cr and 9% Ni), type 304 (19% Cr and 10% Ni), and type 316 (19% Cr and 12% Ni). Additionally, type 316 contains 2–3% Mo which greatly improves the resistance to crevice corrosion in seawater as well as general corrosion resistance. All of the stainless steels offer exceptional improvement in all sorts of atmospheric conditions. They depend for their unusual corrosion resistance on the formation of a passive film, and for this reason are susceptible to pitting. Type 304 stainless, the so-called 18-8 alloy, has very good resistance to moving seawater but does pit in stagnant seawater owing to the development of concentration cells (see Figure 2(**a**) and (**b**)).

Several copper alloys are exceptionally resistant to certain atmospheres. The Cu–Ni alloys, 90% Cu, 10% Ni, and 70% Cu, 30% Ni have outstanding resistance to corrosion in seawater, assuming the Fe content (0.5–1%) is properly controlled. In this application the alloy must resist fouling as well as corrosion. Monel alloy (66.5% Ni, 31.5% Cu) is widely used in marine service where strength is also required. Several copper alloys, silicon bronzes, aluminum bronzes, and manganese bronzes are resistant to severe atmospheric corrosion conditions, and because of their high strength are used as bolts, clamps or load-carrying parts in outdoor environments. Specific alloys have been found suitable for very corrosive environments. For example, Carpenter 20 (20% Cr, 29% Ni, 2.5% Mo, and 3.5% Cu) has outstanding resistance to concentrated sulfuric acid.

For most environments studies have been reported with quantitative data describing the corrosion rate of various materials including a number of corrosion resistant alloys. For example, Table 8 gives weight losses suffered by various corrosion resistant alloys in 28% phosphoric acid, 20–22% sulfuric acid, and 1–15% fluoride (27).

Table 8. Plant Test in Sulfuric Acid Dilution with Recirculated Phosphoric Acid[a]

Materials	Corrosion rate, μm/yr (mpy)	Concentration cell depth, μm(mils)
Carpenter stainless no. 20Cb	28 (1.1)	
Aloyco 20	38 (1.5)	
Incoloy alloy 825	69 (2.7)	127 (5)
Hastelloy alloy C	71 (2.8)	
Illium "G"	76 (3.0)	
Inconel alloy 718[b]	81 (3.2)[c]	
Worthite	109 (4.3)	76 (3)
Incoloy alloy 901[d]	155 (6.1)	127 (5)
Illium "R"	175, 363 (6.9, 14.3)	
Monel alloy K-500[e]	787 (31)	[f]
Monel alloy 400	965 (38)	
Hastelloy alloy B	1980 (78)	
stainless type 317	>3800 (>150) (s)	
stainless type 316	>4600 (>180) (s)	

[a] Phosphoric acid (wet-process) 28% (20% P_2O_5) sulfuric acid 20–22%, fluoride approx 1–1.5%, probably as hydrofluosilicic acid; temperature 82–110°C, average 93°C; and duration of test 42 days, moderate aeration, agitation by convection only.

[b] Composition 52.5% Ni, 18.6% Cr, 18.5% Fe, 5.0% Cb, and 3.1% Mo.

[c] Pitted to a maximum depth of 127 μm (5 mils).

[d] Composition 42.7% Ni, 34.0% Fe, 13.5% Cr, 6.2% Mo, and 2.5% Ti.

[e] Composition 65.0% Ni, 29.5% Cu, 2.8% Al, and 1.0% Fe.

[f] Pitted to a maximum depth of 76 μm (3 mils).

[g] Stress-corrosion cracking around markings.

Corrosion Inhibitors

Inhibitors are defined as chemical substances that, when added in small amounts to the environment in which the metal would corrode, will retard or entirely prevent this corrosion. In this sense, sodium sulfite and hydrazine added to water to remove oxygen, or silica gel to remove water from the atmosphere may be called inhibitors. However, in this article the term inhibitors is restricted to those materials that must interact with the metal surface to prevent corrosion.

The subject of inhibitors from theoretical and applied viewpoint is well covered in a monograph, *Corrosion Inhibitors* (28).

Inhibitors may be discussed as (*1*) inorganic inhibitors, (*2*) organic inhibitors, and (*3*) vapor-phase inhibitors, without any implication that inorganic inhibitors function by a mechanism difference from organic or vapor-phase inhibitors.

Inorganic Inhibitors. Considering first inorganic inhibitors, a subclassification is usually made on the basis of the functioning of the inhibitor with or without oxygen. Inhibitors that can function without oxygen are sometimes called passivators (30). These compounds include chromate and nitrate. They themselves are readily reduced and are able to oxidize the metal surface, usually iron, to form a passive oxide film. Other inorganic compounds required oxygen. These include sodium phosphates, silicates, and borates.

Inhibitors may also be classified in terms of their mechanism, that is, whether they function by influencing the anodic or cathodic side of the electrochemical corrosion cell, although there is not general agreement with regard to a given inhibitor functioning as an anodic or cathodic inhibitor under all conditions of pH, oxygen content, and temperature. However, chromates, nitrites, silicates, phosphates, and borates are usually considered to be anodic inhibitors and those cations that react with the cathodically generated hydroxide to form an insoluble compound, such as Mg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, and Ni^{2+}, are considered to be cathodic inhibitors; thus, calcium polyphosphate [*7758-87-4*] may be viewed as a cathodic inhibitor. The differentiation is made by the direction in which the potential moves upon the addition of the inhibitor to the system. An anodic inhibitor will cause the potential to move in the positive direction, the cathodic inhibitor will move the potential in the negative direction, that is, towards the equilibrium potential of the anodic reaction.

To inhibit corrosion in cooling waters, polyphosphates, nitrites, and chromates have been used, although in recent years the use of the latter has been discouraged even in closed systems because of environmental considerations. In municipal water supplies low concentrations (eg, 10–200 ppm) of polyphosphate and silicate have been employed (see Water, municipal water treatment). In some hot water systems borax [*12447-40-4*] has been used, and in common with some other systems, an adjustment in pH to the neutral range has been required (see Water, industrial water treatment). The antifreeze (qv) mixtures used in automobile cooling systems present a difficult problem because within the system several metals, iron, copper, lead–tin solders, aluminum, as well as rubber are in contact, encouraging galvanic corrosion. The successful formulations are proprietary, but some contain borates, polyphosphates, and mercaptobenzothiazole [*1321-08-0*] (an organic inhibitor). In acid solutions as, for example, those used in the pickling of steel, organic compounds have been used most successfully (see Metal surface treatments).

The concentrations required for inhibition are dependent on such factors as the presence or absence of chloride ion, the temperature, and the movement of the corroding solution; however, usually the effective concentration for inorganic inhibition falls in the range of several hundred ppm. Oxidizing inhibitors usually function at considerably lower concentrations than nonoxidizing inhibitors. It should be noted that, with respect to the oxidizing anions such as chromate, nitrite, molybdate, and tungstate there exists a critical concentration (31). These along with the concentrations to achieve inhibition are shown in Figure 11 (32).

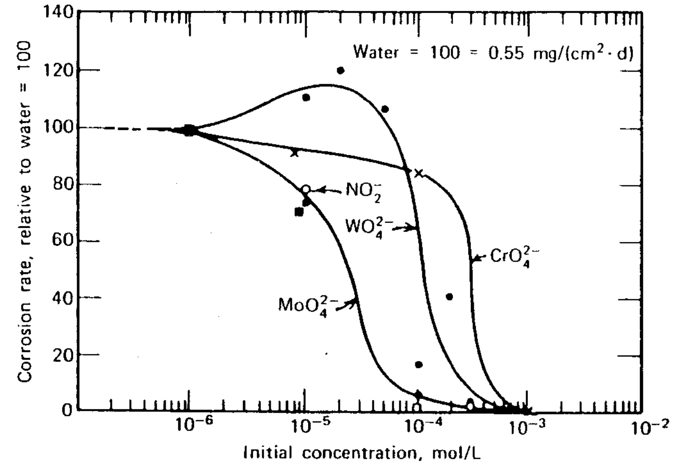


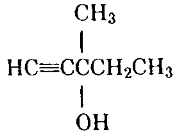
Figure 11. Concentrations of several inhibitors required to achieve inhibition (32).

Organic Inhibitors. A large number of organic compounds have been used as organic inhibitors; one review (33) lists 141 basic structures that have been utilized. Organic inhibitors and their effectiveness have been systematically discussed (34) on the basis of the type of bonding the organic molecule achieves with the metal. It is generally recognized that to be effective the compound must be adsorbed, but the type of adsorption bond varies with the chemical configuration of the molecule. The main types of adsorption involve electrostatic adsorption, chemisorption, and π-bond (delocalized electron) adsorption. Foroulis (34) cites examples of each type of adsorption. Inhibition by electrostatic adsorption is illustrated by aniline [*62-53-3*] and substituted anilines, pyridine [*25275-41-6*], butylamine [*109-73-9*], benzoic acid [*65-85-0*], and substituted benzoic acids and compounds such as benzenesulfonic acid [*98-11-3*].

Some of the types of compounds that function through electrostatic adsorption may also function by a chemisorption process. Chemisorption is most evident with nitrogen or sulfur heterocycles. Benzotriazole [*27556-51-0*] and tolytriazole[*29385-43-1*], both effective inhibitors of copper corrosion, are believed to operate through chemisorption as does 0.1 *M* butylamine which is effective in inhibiting the corrosion of iron in concentrated perchloric acid. However a single compound may apparently utilize different mechanisms to be effective.

The interaction of delocalized electrons (π-bond orbital interaction) with the metallic surface may be quite effective. Data on the corrosion inhibition of 1020 carbon steel in 2.8 *N* HCl at 65°C, given in Table 9 (35), illustrates this effect. As the structure goes from the single to the double to the triple bond the opportunity for π-bond interaction with the metal increases. However, as indicated by the last compound, such factors as steric interference may decrease the efficiency of inhibition.

Table 9. Corrosion Inhibition Data with 1020 Carbon Steel[a]

Inhibitor[b]	CAS Registry No.	Corrosion rate, metal loss in mg/(dm²·d)
blank		>48,900
$CH_3CH_2CH_2OH$	*[71-23-8]*	>48,900
$CH_2{=}CHCH_2OH$	*[107-18-6]*	13,200
$HC{\equiv}CCH_2OH$	*[107-19-7]*	146
 $HC{\equiv}CC(CH_3)(OH)CH_2CH_3$	*[77-75-8]*	1,956

[a] In 2.8 *N* HCl, 65°C.

[b] 0.4 wt %.

Generally, the concentration of organic inhibitor is substantially higher than that required for inorganic inhibitors such as chromates. The corrosion of iron in 6 *N* HCl at 30°C is inhibited by nonamethyleneimine *[4396-27-4]*; 1% addition reduces the corrosion current by an order of magnitude (36). Typical pickling inhibitors include quinoline *[91-22-5]* and substituted quinolines, thiourea *[62-56-6]*, dihexylamine *[143-16-8]*, and tolualdehyde *[1334-78-9]*. A number of organic inhibitors have been effective in reducing corrosion of tin plate in citric acid. These include diphenylurea *[102-07-8]*, carbon disulfide *[75-15-0]*, and allylthiourea *[109-57-9]* (37). In boiler treatment, so-called filming amines, such as octadecylamine *[123-30-1]* and hexadecylamine *[143-27-1]* are effective in retarding corrosion by carbonic acid.

Vapor-Phase Inhibitors. Vapor-phase inhibitors are volatile compounds containing one or more functional groups capable of inhibiting corrosion. The principle is to saturate with the volatile compound the vapor in which the metal object resides. The compound is adsorbed and, in the presence of atmospheric moisture, dissociates to develop functional groups on the surface that retard corrosion. The surface of the metal does not have to be prepared in any special way, as is the case with electroplating, and the inhibitor will function even if the surface is oxidized or rusted before application. The inhibitor will not remove the rust but will prevent further rusting.

The operation of volatile inhibitors has been related to electrochemical theory by pointing out that the inhibitors operate by altering the electrochemical kinetics in a fashion similar to aqueous corrosion (30). The inhibitor must have three properties to be effective: (*1*) it must contain certain functional groups to provide inhibition; (*2*) it must have a vapor pressure above a minimum value; and (*3*) it must be adsorbed on the metal surface. Some of the classes of compounds that have furnished successful volatile inhibitors have been tabulated (38). These include: (*1*) amine salts with nitrous or chromic acids; (*2*) amine salts with carbonic, carbamic, acetic, and substituted or unsubstituted benzoic acids; (*3*) organic esters of nitrous, phthalic, or carbonic acids; (*4*) primary, secondary, and tertiary aliphatic amines; (*5*) cycloaliphatic and aromatic amines; (*6*) polymethylene amines; (*7*) mixtures of nitrites with urea *[57-13-6]*, urotropine *[100-97-0]*, and ethanolamines; (*8*) nitrobenzene *[98-95-3]* and 1-nitronaphthalene *[86-57-7]*.

Dicyclohexylamine nitrite *[3129-91-7]* has been used commercially for many years and a number of volatile compounds are available commercially as powders or tablets to be included in a package containing metallic parts to be protected. The system must be closed to retain the volatile compound, but this is not a significant problem and objects as large as the interior of an ocean-going tanker have been treated by this technique.

A large number of commercial inhibitors and inhibitor formulations are available; some of these are listed along with their intended application in Table 10.

Table 10. Typical Commercial Inhibitors

Type of inhibitor	Proprietary name	Application
chromate based (10–20 ppm as CrO_4)	CWT 102[a]	for open, recirculating cooling system
nonchromate, phosphate based, 10–12 ppm as PO_4	Drewgard 180[a]	for open, recirculating cooling system
chromate (200–500 ppm as CrO_4)	DEWT-L[a]	closed, recirculating cooling system
nonchromate, organic based	Drewgard 100[a]	closed, recirculating cooling system
phosphate (1–10 ppm as PO_4)	Drewgard 120[a]	once-through cooling system
silicate (8–10 ppm as SiO_2)	CIL[a]	once-through cooling system
sodium molybdate (3 ppm)	Molybdate Corrosion Inhibitor[b]	for ferrous and nonferrous metals, cooling and heating systems, hydraulic fluids
organic corrosion inhibitor (formulation of alkylthiophosphate, phosphate esters, and zinc salts)	Tol-Aeromer[c] ACW-11, ACW-15, ACW-16,	for recirculating cooling systems, heat exchangers
chromate, phosphate, and zinc salts	TCW-14[c], TCW-15	corrosion and fouling in piping and heat exchange recirculating cooling water systems
organic corrosion inhibitor (organic phosphate ester)	Tol-Aeromer[c] ACW-18	for recirculating cooling systems
organic corrosion inhibitor (no phosphorus compounds) (2000–4000 ppm)	Tol-Aeromer[c] ACW-22	for closed water systems
buffered organic corrosion and deposit inhibitor	Tol-Aeromer[c], ACW-61	for closed systems, with ferrous and nonferrous metals
chromate and zinc salts (100 ppm)	TCW-10[c], TCW-11, TCW-12	for corrosion and fouling in recirculating cooling water systems
vapor phase inhibitor	NI-22790[d]	for packaging, shipping, and storage of ferrous and nonferrous parts
vapor phase inhibitor	Cor-tab[d], CT-25, CT-50, CT-10	these are vapor phase corrosion inhibitors in tablet form
fatty acid–fatty amine	Cortron R-66[e]	for oil flow lines
quaternary ammonium chloride	Cortron RU-14[e]	for gas lines
fatty imidazoline–fatty acid salt	Cortron R-2258[e]	for oil wells

[a] Marketed by Drew Chemical Corporation, Boonton, N.J.
[b] Marketed by Climax Molybdenum Co., Greenwich, Conn.
[c] Marketed by Tretolite Division, Petrolite Corp., St. Louis, Mo.
[d] Marketed by Northern Instrument Co., St. Paul, Minnesota.
[e] Marketed by Champion Chemicals, Inc., Houston, Texas. (Other commercial suppliers of corrosion inhibitors or treatments are Betz Laboratories, Trevose, Pa.; Nalco Chemical Co., Oak Brook, Illinois; Calgon Corporation, Pittsburgh, Pa.; and Mogul Division of the Dexter Corporation, Chagrin Falls, Ohio.)

Coatings for Protection Against Corrosion

The coatings useful for the protection of metals against corrosion may be characterized by the temperature at which they are applied, whether or not they require

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Sodium Chloride. Sodium chloride, a corrodent of many materials, is the archetype contaminant and has been studied more than other salts. The solubility of sodium chloride in superheated steam is shown at the conditions of a typical steam turbine expansion in Figure 14. The solubilities were measured in the region of higher solubility (9). As the steam expands, sodium chloride becomes considerably less soluble. The solubility, S, in parts per billion (ppb) can be represented by equation 3:

$$\log S = 3.36 \log V + 1760/T + 4.45 \qquad (3)$$

where V is the molar volume of steam in L/mol and T is the temperature in K. There is a combined effect of decreasing density and decreasing temperature (9).

Silica. Silica is not actually a corrodent of turbines. However, it can deposit on and cause blocking of turbine passages, thus reducing turbine capacity and efficiency. As little as 76 μm (3 mils) of deposit can cause measurable loss in turbine efficiency. Severe deposition can also cause imbalance of the turbine and vibration. The solubility in steam and water is shown in Figure 15, as is a typical steam turbine expansion. Silica is not a problem except in low pressure turbines unless the concentrations are extraordinarily high.

Moderately Volatile Materials. For moderately volatile materials, such as the amines commonly used in feedwater and boiler water chemical treatment, the distribution ratios vary from 0.1 to 30; for gases, the ratios are much higher. The distribution ratios of amines and organic acids are generally temperature-dependent. The distribution ratios for ammonia [*7664-41-7*], morpholine [*110-91-8*], and acetic acid [*64-19-7*] are shown in Figure 16 as examples.

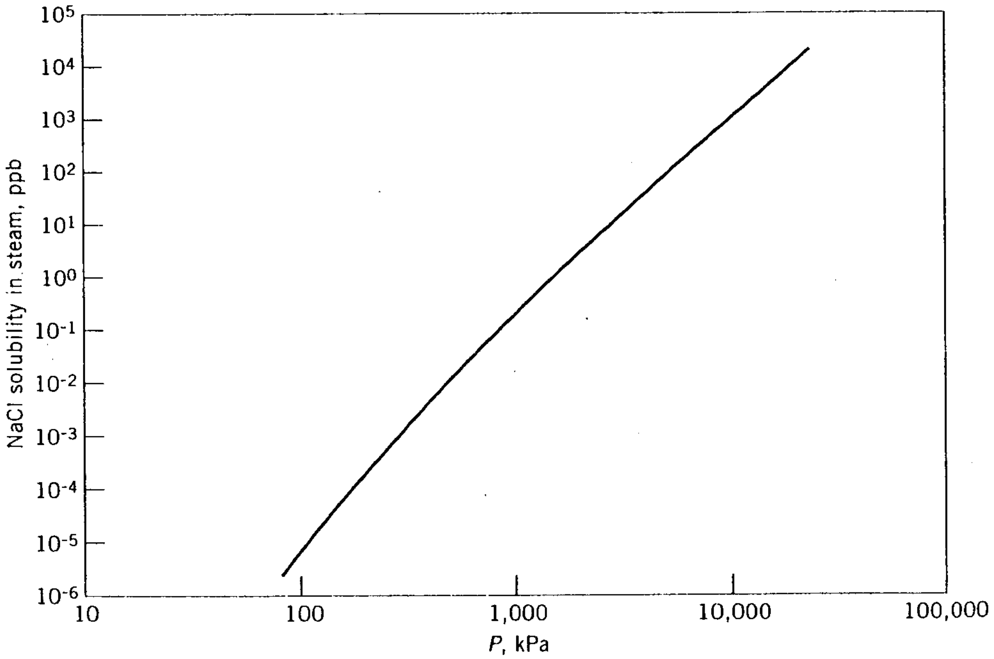

Fig. 14. Solubility of NaCl as a function of pressure on typical turbine expansion line (9). To convert kPa to psi, multiply by 0.145.

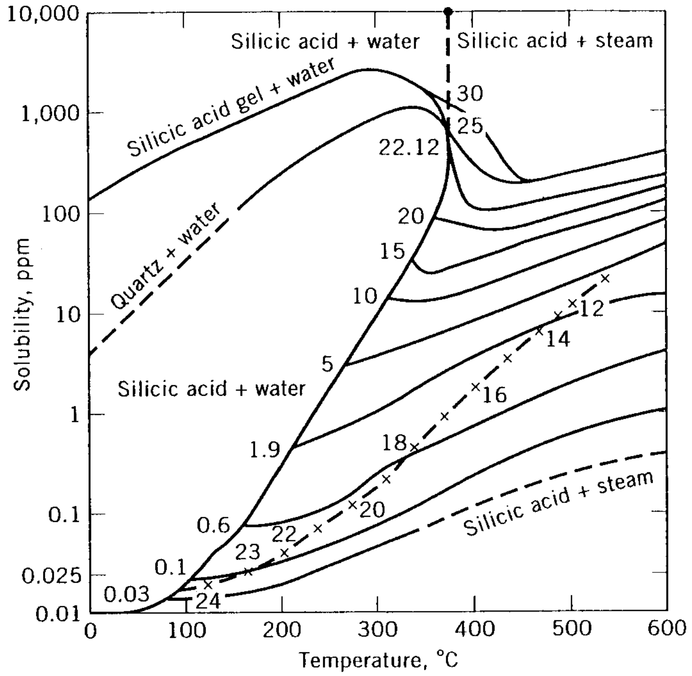

Fig. 15. Silica solubility diagram, where (–×–) is the turbine expansion line and (●) is the critical point (10). Numbers represent pressure in MPa. To convert MPa to psi, multiply by 145.

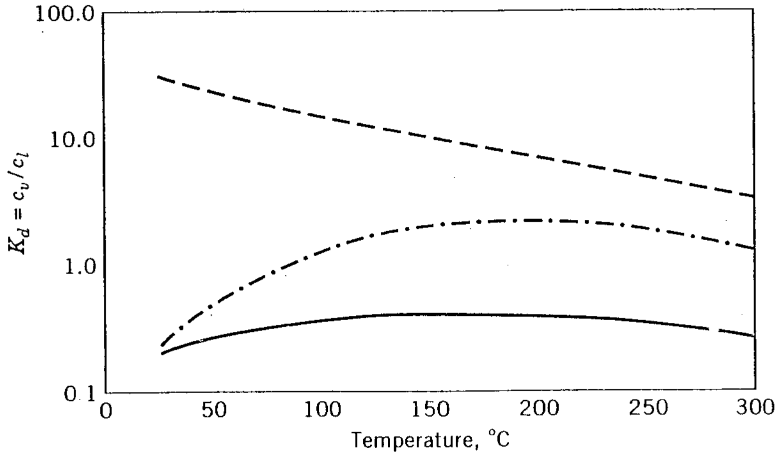

Fig. 16. Distribution of (– – –) ammonia, (– · –) morpholine, and (——) acetic acid between water and steam (7).

Gases. At low temperatures and pressures, most gases are relatively insoluble in water and tend to appear in the steam phase. Only those gases that ionize to some extent violate this rule. However, as the pressure approaches the critical point, the solubility of gases increases.

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temperature feedwater heater or collected and pumped forward into the main feedwater stream. In a direct-contact or deaerating heater, the water is sprayed through a steam space and flows down trays in thin layers. Steam is admitted at the bottom and flows upward countercurrent to the water. Dissolved gases are removed in direct-contact heaters and must be vented.

Condenser. Water-cooled condensers are constructed of tubes between tubesheets (Fig. 22). Cooling water is pumped from the source into the inlet waterbox, through the tubes, and through the outlet waterbox. Tight joints between the tubes and tubesheet are necessary to prevent ingress of the cooling water. Total cooling water leakage as small as 4 L/d of fresh water can produce unacceptable impurity concentrations in feedwater for nuclear steam generators. Careful selection of condenser materials is required for long-term reliability. Double tubesheets having condensate between the two sheets are a method of reducing the likelihood of cooling water leaks. The cooling water may be drawn from lakes or rivers or may be recirculated from cooling towers. Cooling water chemistry is complex because of precipitation and microbiological considerations. It is treated in handbooks by water treatment chemical vendors (22–24) (see WATER, INDUSTRIAL WATER TREATMENT).

Air-cooled condensers are used more frequently in the 1990s as cooling water sources are being exhausted. Air-cooled condensers consist of large numbers of finned tubes. Air is forced past the outside of the tubes and the steam condenses on the inside. Cooling water leakage is not a problem when air-cooled condensers are used, but air in-leakage is a bigger problem than for water-cooled condensers.

Water Chemistry in Steam-Generating Systems. *Specifications. Steam Purity.* The usual function of steam purity limits is to protect the turbine from deposition and subsequent corrosion. In systems where the steam is used

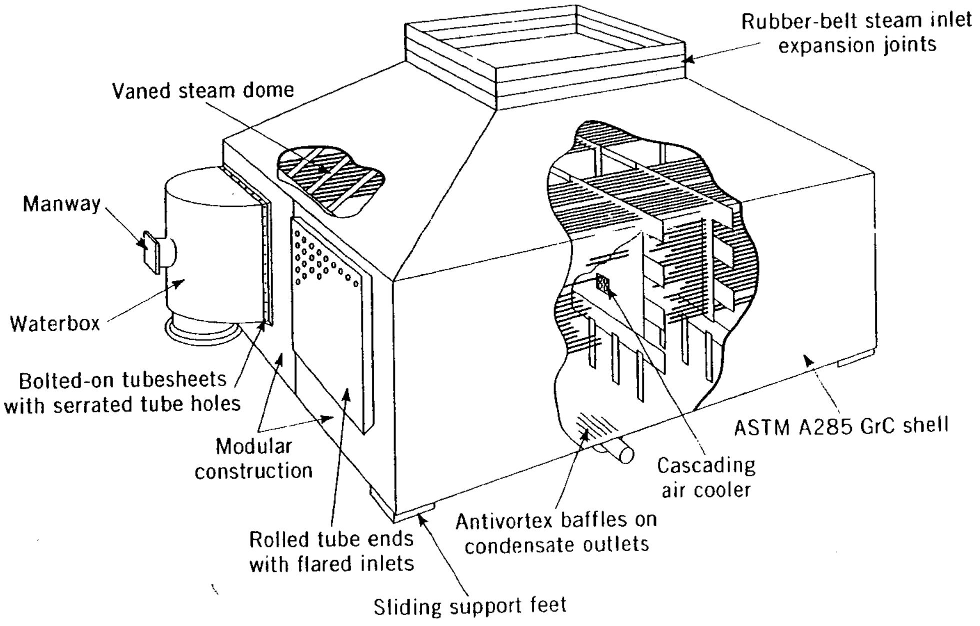

Fig. 22. Schematic of a condenser.

for chemical processes, the specific process may create additional requirements for steam purity. For instance, in food processing (qv), regulations may limit or prohibit hydrazine in the steam, so ascorbic acid or sodium sulfite must be used as an oxygen scavenger. When steam is sent to processes and returned as condensate, it may be necessary to add pH control agents to the steam to control corrosion at various points in the process and condensate return system. Table 1 gives typical steam purity recommendations for steam turbine protection. The recommendations vary, depending on whether the feedwater treatment generates an oxidizing or a reducing environment. In addition to the normal limits, most vendors have time-limited excursion ranges, which provide tolerance for upset conditions and the higher impurity concentrations commonly found on the startup of a boiler system. The recommendations are derived from a blend of theoretical considerations of solubility of salts in steam, practical limits on water purity, and experience with what has proved successful. The development of steam purity limits is available (14,15).

Boiler Water. The steam purity limits define boiler-water limits because the steam cannot be purified once it leaves the boiler. For a once-through boiler, the boiler water must have the same specifications as the steam. A recirculating boiler is a still, and there can be considerable purification of the steam as it boils and is separated from the water in the steam drum. The process of separation is not perfect, however, and some water is entrained in the steam. This water, called mechanical carryover, contains impurities in the same proportions as the boiler water, and its contribution to steam impurity is in those proportions. Typical mechanical carryover is less than 0.25% and often less than 0.1%, but operating conditions in the boiler can affect the mechanical carryover. In addition to mechanical carryover, chemicals can be carried into the steam because of solubility. This is called vaporous carryover. Total carryover is the sum of mechanical and vaporous carryover. The boiler-water specification must be such that the total carryover conforms to the steam purity requirements. For salts, such as sodium phosphate and sodium chloride, vaporous carryover is not a significant problem below approximately 15 MPa (2175 psia). As boiler pressures approach the critical point, vaporous carryover increases rapidly. Above 15 MPa (150 bar), boiler solids concentrations must be carefully controlled to minimize vaporous carryover. Most boilers operating over 18 MPa (180 bar) use all volatile

Table 1. Steam Purity Recommendations

Parameter	Environments	
	Reducing	Oxidizing
conductivity, μS/cm		
hydrogen cation-exchanged	0.1–0.3	<0.2
degassed cation	0.15–0.35	
sodium, ppb	3–10	
silica, ppb	10–20	
iron, ppb	20	
copper, ppb	2	
chloride, ppb	5–10	
sulfate, ppb	3–6	
oxygen, ppb		50–150

treatment to prevent deposition of salts in turbines. Boiler-water limits for utility boiler are listed in Table 2. Recommendations from American Boiler Manufacturers' Association (ABMA) for boiler-water limits for drum-type boilers and associated steam purity for watertube boilers are listed in Table 3.

In addition to the requirement to conform to steam purity needs, there are concerns that the boiler water not corrode the boiler tubes nor produce deposits, known as scale, on these tubes. Three important components of boiler tube scale are iron oxides, copper oxides, and calcium salts, particularly calcium carbonate [*471-34-1*]. Calcium carbonate in the feedwater tends to produce a hard, tenacious deposit. Sodium phosphate is often added to the water of recirculating boilers to change the precipitate from calcium carbonate to calcium phosphate (see also WATER, INDUSTRIAL WATER TREATMENT).

Feedwater. The feedwater for a steam cycle must be purified. The degree of purity depends on the pressure of the boiler. Higher pressure boilers require higher feedwater purity. There is some trade-off between feedwater purity and boiler blowdown rate. However, increasing blowdown rate to compensate for lower feedwater purity is expensive, because blowdown water has been heated to the saturation temperature. Typical feedwater specifications for utility boilers are given in Table 4. To some extent turbine steam purity requirements determine the feedwater purity requirements. The boiler-water silica required to maintain adequate steam purity for higher pressure steam turbines is considerably less than the boiler could tolerate if deposition in the boiler were the only issue.

Makeup. Makeup water is the water supplied to replenish the steam system for any losses. In most systems it is introduced into the condenser or the feed pump suction. In steam systems where the makeup is a small fraction of the total feedwater, its purity may be somewhat lower than the feedwater requirement because it is diluted by condensate. In systems where there is little condensate return, such as heating steam supplies, the makeup purity must be essentially the same as the feedwater.

Water Treatment. Water and steam chemistry must be rigorously controlled to prevent deposition of impurities and corrosion of the steam cycle. Deposition on boiler tubing walls reduces heat transfer and can lead to overheating, creep, and eventual failure. Additionally, corrosion can develop under the deposits and lead to failure. If steam is used for chemical processes or as a heat-transfer medium for food and pharmaceutical preparation there are limitations on the additives that may be used. Steam purity requirements set the allowable impurity concentrations for the rest of most cycles. Once contaminants enter the steam, there is no practical way to remove them. Thus all purification must be

Table 2. Boiler-Water Limits for Utility Boiler[a,b]

Elements, ppm	All-volatile treatment	Phosphate
sodium	0.7	1.7
chloride	0.28	0.9
sulfate	0.28	1.6
silica	13	13
phosphate		2.2

[a] At 17.2 MPa (2500 psia). [b] Ref. 14.

Table 3. ABMA Recommended Boiler-Water Limits[a]

Drum pressure, MPa[b]	Boiler-water limits, ppm: Total dissolved solids[c]	Boiler-water limits, ppm: Total alkalinity	Boiler-water limits, ppm: Suspended solids[c]	Steam limits, ppm: Expected total dissolved solids[c,d]
		Drum boilers		
0.1–2.2	700–3500	140–170	15	0.2–1.0
2.2–3.2	600–3000	120–600	10	0.2–1.0
3.2–4.2	500–2500	100–500	8	0.2–1.0
4.2–5.3	400–2000	80–400	6	0.2–1.0
5.3–6.3	300–1500	60–300	4	0.2–1.0
6.3–7.0	250–1250	50–250	2	0.2–1.0
7.0–12.5	100	[e]	1	0.1
12.5–16.3	50		[f]	0.1
16.3–18	25		[f]	0.05
18.0–20.1	15		[f]	0.05
		Once-through boilers		
≥9.8	0.05	[f]	[f]	0.05

[a] Ref. 16.

[b] To convert MPa to psi, multiply by 145.

[c] Values are maximum.

[d] Values are exclusive of silica.

[e] Dictated by boiler-water treatment.

[f] Not applicable.

Table 4. Utility Feedwater Specifications for Normal Operation

Parameter	Reducing chemistry		Oxidizing chemistry
	Recirculating boiler	Once-through boiler	Once-through boiler
pH			
all-ferrous metallurgy	9.0–9.6	9.0–9.6	8.0–8.5
mixed Fe–Cu metallurgy	8.8–9.3	8.8–9.3	
cation-exchanged conductivity, μS/cm	≤0.2	≤0.2	≤0.15
iron, ppb	≤10	≤10	≤5
copper, ppb	≤2	≤2	
oxygen, ppb	≤5	≤5	50–150

[a] Refs. 14 and 17.

carried out in the boiler or preboiler part of the cycle. The principal exception is in the case of nuclear steam generators, which require very pure water. These tend to provide steam that is considerably lower in most impurities than the turbine requires. A variety of water treatments are summarized in Table 5. Although the subtleties of water treatment in steam systems are beyond the scope of this article, uses of various additives may be summarized as follows:

Water treatment additive	Effect
sodium orthophosphate	pH control; hardness precipitation
sodium hydroxide, lithium hydroxide	pH control (acid neutralization)
neutralizing volatile amines (ammonia, morpholine, cyclohexylamine, diethanolamine, ethanolamine, etc)	once-through and pressurized-water reactor cycles, high heat flux steam generators; control of preboiler corrosion-product generation and transport; no control of scale formation by feedwater contaminants
hydrazine	oxygen scavenging
sodium sulfite	oxygen scavenging
sludge conditioners	dispersion of sludge for easy removal by blowdown in drum boilers, inhibiting of scale formation
synthetic sulfonated polymer, synthetic carboxylated polymer, polyacrylic acid	<6.9 MPa (1000 psi)
carboxymethyl cellulose, organophosphonate	<4.1 MPa (600 psi)
lignin	<2.1 MPa (300 psi)
oxygen or hydrogen peroxide	improve surface passivation in all-ferrous high purity water systems
filming amines (octadecylamine and some of its salts)	surface protection against condensate corrosion
antifoams (polyglycols, polyamides)	reduce foaming and carryover in boilers

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Table 5. Water Treatment Schemes

Program	Characteristics: Favorable	Characteristics: Unfavorable
phosphate		
conventional, $Na_3PO_4(+NaOH)$	hardness salts converted to a form readily removed by bottom blowdown; relatively high levels of suspended solids successfully controlled; acids neutralized; surface passivation by PO_4^{3-}	high pressure boilers cannot tolerate intentional formation of boiler sludge; required alkalinity levels are too high for operation >10.4 MPa (1500 psig); oil or organic contamination produces highly adherent deposit; possible under-deposit corrosion by NaOH
coordinated, $[Na]:[PO_4] < 3$	caustic corrosion may be eliminated; deposit form makes for easy removal; produces low solids levels and high steam purity; acids neutralized; surface passivation by PO_4^{3-}	in boilers containing deposits, chemical interaction of iron and phosphate can lead to caustic corrosion; at very low $[Na]:[PO_4]$ molar ratios (<2.1), corrosion by phosphoric acid possible
congruent, $2.6 < [Na]:[PO_4] < 2.8$	caustic and acid corrosion eliminated; deposit form makes for easy removal; produces low solids levels and high steam purity; acids neutralized; surface passivation by PO_4^{3-}	control of the $[Na]:[PO_4]$ molar ratio may be difficult; continuous feed and blowdown may be required
NaOH or LiOH	acid neutralization	can cause rapid corrosion when concentrated in high quality regions or under deposits; vaporous carryover in steam at higher pressures; difficult to analyze
chelates, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA)	optimum heat-transfer and boiler efficiency obtained under good feedwater-quality conditions; elimination of boiler sludge prevents formation of adherent deposits involving oil/organics	inability to analyze free chelant residual accurately can lead to overfeed and subsequent corrosion[a]; does not complex iron or copper under normal boiler-water pH conditions; presence of oxygen in boiler water can cause dechelation and excessive corrosion; limited to lower pressure boilers (see text)

Table 5. (*Continued*)

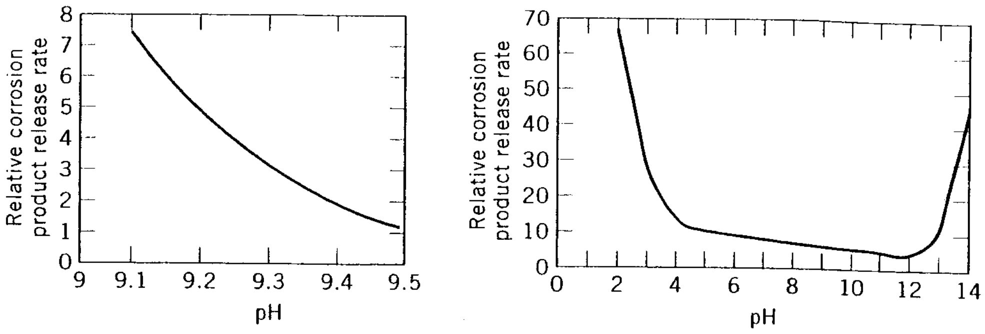
Program	Characteristics	
	Favorable	Unfavorable
all-volatile[b]	near-zero solids in boiler water and high purity steam realized under ideal feedwater conditions; having some corrosion protection; no carryover of solids; no surface concentration; condenser leakage detection by sodium measurement; boiler deposition of corrosion products easy to remove by chemical cleaning	feedwater contamination may exceed inhibiting ability of volatile fed, leading to boiler corrosion; introduction of contaminants into feedwater produces deposits that may be hard to remove; marginal acid neutralization, particularly when using ammonia in wet steam regions; interference with condensate polishing; corrosion of copper alloys by ammonia and oxygen; organic acid decomposition products of organic amines
oxygenated treatment	no interference of additives with condensate polishing; low corrosion rates of ferritic steels	requires extremely low concentrations of impurities in feedwater; no corrosion protection in case of an upset; corrosion of copper alloys; precise control required

[a] Condition is heightened when treatment is applied to deposit-bearing boiler.

[b] Such as ammonia, morpholine, cyclohexylamine, and ethanolamine (ETA).

Reducing Chemistry. Most steam systems are maintained in a reducing state to avoid oxidation of the steel piping and other components. Oxidation is further suppressed by raising the pH, which is commonly controlled by using ammonia, although organic amines, such as morpholine, cyclohexylamine, ethanolamine, and dimethylamine, are also used. Organic amines are not generally employed for systems having superheat temperatures ≥538°C (1000°F) because these tend to decompose to organic acids, which can be corrosive. Most feedwater is treated with hydrazine to reduce the oxygen concentration to the 1–5-ppb range. Carbohydrazide, hydroquinone, and methylethylketoxime are also used as oxygen scavengers. In plants where the steam may be in contact with food, sodium sulfite, ascorbic acid, or erythorbic acid is commonly used as an oxygen scavenger.

Feedwater treatment is designed to protect the feedwater system and, to some extent, the boiler. Most systems contain carbon steel piping. Carbon steel corrosion (Fig. 23a) is considerably slower at a pH between 9.0 and 11.0. In



(a) (b)

Fig. 23. Corrosion rates of carbon steel as a function of pH of (**a**) the feedwater (18) and (**b**) boiler conditions (19).

all-ferrous feedwater systems, the preferred pH range is therefore 9.2 to 9.6, although some systems are operated at a pH as high as 10. In systems where copper alloys are present, high concentrations of ammonia accelerate corrosion of the copper alloys. In those systems the preferred pH is 8.8–9.2.

For once-through boilers, the treatment must be without solid residues, so all-volatile treatment (AVT) is used. AVT, which is also used in some drum boiler systems, relies on the feedwater chemical additives, ammonia and hydrazine, to provide water appropriate to the boiler. Because the additives are volatile, they do not accumulate in the boiler and provide only minimal protection during contaminant ingress. Most plants using AVT have some form of condensate polisher to remove impurities from the condensate.

Boiler tubes are susceptible to corrosion owing to contaminant ingress. Adding solid buffers to the boiler water can reduce corrosion. Figure 23**b** shows the rate of carbon steel corrosion as a function of pH at boiler conditions. If feedwater impurities or faulty chemical additions cause the boiler pH to move outside the acceptable range, corrosion can be rapid and boiler tube failure may occur in a matter of hours. If the boiler does not fail immediately, it can also be damaged by hydrogen embrittlement, which makes it subject to failures during thermal transients, such as startup.

In drum boilers sodium hydroxide (caustic), sodium phosphate, or both may be added for pH and scale control. Sodium hydroxide is used more in Europe than in the United States, where sodium phosphate treatment is usually preferred. In boilers operating above 4 MPa (580 psia), caustic concentrations must be carefully controlled to prevent highly corrosive deposits from forming. In the lowest pressure boilers, phosphate treatment may be used to compensate for lower purity feedwater. As the boiler pressure increases, the allowable phosphate concentration decreases, and at 16.5 MPa (2400 psia) or above, equilibrium phosphate treatment may be used. In this treatment, caustic is added to a low phosphate concentration in the boiler to maintain the proper pH (20).

In lower pressure boilers a variety of additional treatments may be appropriate, particularly if the steam is used in chemical process or other nonturbine application. Chelants and sludge conditioners are employed to condition scale and enable the use of less pure feedwater. When the drum pressure is less than

7 MPa (1015 psia), sodium sulfite may be added directly to the boiler water as an oxygen scavenger. It has minimal effect on the oxygen concentration in the system before the boiler.

The selection of boiler-water treatment is also dependent on the type of cooling water. When cooling water reaches the boiler, various compounds precipitate before others. For instance, seawater contains considerable magnesium chloride. When the magnesium precipitates as the hydroxide, hydrochloric acid remains. In some lake waters, calcium carbonate is a significant impurity. When it reaches the boiler, carbon dioxide is driven off in the steam and calcium hydroxide is formed. If the cooling water tends to form acid in the boiler, either caustic or phosphate may be added to counteract the effect. When the cooling water tends to form base, only phosphate treatment is appropriate. Many drum boilers that are operated on AVT have provision for phosphate or caustic treatment during condenser leaks because the amines used in AVT have neither significant buffering capacity nor precipitate conditioning properties in the boiler.

Oxidizing Chemistry. In high pressure boilers systems having the ability to maintain hydrogen cation-exchanged conductivity near or below 0.1 μS/cm, the feedwater may be treated with oxygen. Oxygen is added either as gaseous oxygen or as hydrogen peroxide. The pH may be neutral or elevated with ammonia. The goal of this treatment is to maintain all iron alloy surfaces in a passivated state. The rate of carbon steel corrosion as a function of oxygen is shown in Figure 24. At the low (0.1 μS/cm) cation conductivity, the corrosion rate drops over an order of magnitude as the oxygen concentration is increased from 0.02 to 0.2 ppm. When higher anion concentrations inhibit passivation, the increased oxygen causes faster corrosion. Oxygenated water treatment has been used in Germany since the 1970s and is becoming widespread throughout the world. This treatment regime requires systems having no copper alloys. This practice is most advantageous for once-through boiler systems. In recirculating boiler systems, it is very difficult to maintain the hydrogen cation-exchanged conductivity low enough in the boiler water. Thus the oxygen must be flashed in the drum to prevent boiler corrosion. Nonetheless, some recirculating systems have been successfully operated on oxygenated water treatment.

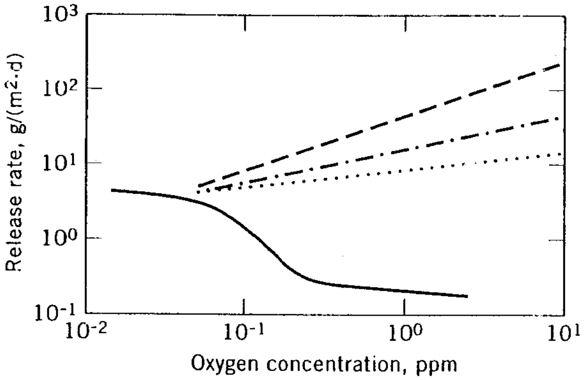


Fig. 24. Corrosion rates of carbon steel as a function of oxygen concentration at cation conductivity values of (——) 0.1, (····) 7, (–·–) 87, and (– – –) 850 μS/cm (21).

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STEARIC ACID. See CARBOXYLIC ACIDS.

STEATITE. See TALC.

Gen'l

EIGHTH EDITION—1980

Library of Congress Catalog Card Number: 79-56368
Second Printing 1982

BETZ LABORATORIES, INC.
Trevose, PA 19047

Previous Editions

First Edition, 1942
Second Edition, 1945
Third Edition, 1950
Fourth Edition, 1953
Fifth Edition, 1957
Sixth Edition, 1962
Seventh Edition, 1976

Printed in U.S.A.

ACKNOWL

This handboo
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tions to this E

J. P. Antisavag
R. Bauers
J. S. Cardarelli
W. R. Cook
G. K. Davisso
J. M. Donohue
P. L. Friend
C. C. Hall
R. T. Houser
E. D. Jackson
A. T. Kashuba

We also thank t
Editorial Revie
nating and revi

A. C. Becker
E. J. Bockowski
J. M. Donohue
P. J. Guagnano
S. L. Hill

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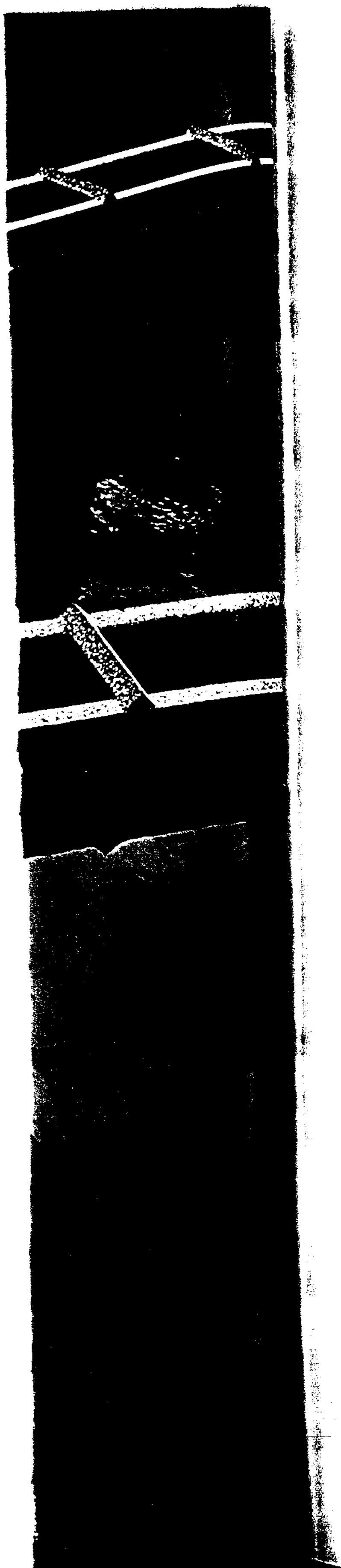

Aeration is a unit process in which air and water are brought into intimate contact. This is usually accomplished by directing the water downflow countercurrent to the air flow which may be atmospheric or forced-draft. The air-water contact time and the air-water volume ratio (standard cubic feet/minute per gallon/minute) must be sufficient for equilibrium to be established.

Aeration is used for the following:

1. carbon dioxide reduction (decarbonation),
2. ammonia and hydrogen sulfide reduction (stripping), and
3. oxidation of iron and manganese found in many well waters (oxidation tower).

IRON AND MANGANESE OXIDATION

As present in well waters, iron and manganese are in the soluble ferrous and manganous bicarbonate forms. The object in aerating water containing these metals is to saturate the water with oxygen to promote the following reactions:

$$\underset{\text{ferrous bicarbonate}}{4Fe(HCO_3)_2} + \underset{\text{oxygen}}{O_2} + \underset{\text{water}}{2H_2O} = \underset{\text{ferric hydroxide}}{4Fe(OH)_3} + \underset{\text{carbon dioxide}}{8CO_2}$$

$$\underset{\text{manganese bicarbonate}}{2Mn(HCO_3)_2} + \underset{\text{oxygen}}{O_2} = \underset{\text{manganese dioxide}}{2MnO_2} + \underset{\text{carbon dioxide}}{4CO_2} + \underset{\text{water}}{2H_2O}$$

The oxidation products, ferric hydroxide and manganese dioxide, are insoluble and are removed by filtration following aeration.

Occasionally, stronger oxidants such as chlorine (Cl_2) or potassium permanganate ($KMnO_4$) may be used following aeration to insure complete oxidation.

Figure 3-1. Natural aeration in streams.

DISSOLVED GAS REDUCTION

Gases dissolved in water follow the principle that the solubility of a gas in a liquid (water) is directly proportional to the pressure of the gas above the liquid at equilibrium. This is known as Henry's Law and may be expressed as follows:

$$C_{total} = kP$$

where C_{total} = total concentration of the gas in solution

P = pressure of the gas above the solution

k = a proportionality constant known as Henry's Law Constant

However, the gases frequently encountered in water treatment (with the exception of oxygen) do not follow Henry's Law because, when dissolved in water, they ionize. For example:

(1)	H_2O -	CO_2	$\rightleftharpoons$	H^-	-	HCO_3^-
	water	carbon dioxide		hydrogen ion		bicarbonate ion
(2)		H_2S	$\rightleftharpoons$	H^-	-	HS^-
		hydrogen sulfide		hydrogen ion		hydro sulfide ion
(3)	H_2O -	NH_3	$\rightleftharpoons$	NH_4^-	+	OH^-
	water	ammonia		ammonium ion		hydroxide ion

Carbon dioxide, hydrogen sulfide, and ammonia are soluble in water to the extent of 1700, 3900 and 531,000 ppm, respectively. Rarely are these concentrations encountered except in certain process condensates. The partial pressure of each of these gases in a normal atmosphere, however, is practically zero. Consequently, the establishment of a state of equilibrium between water and air by means of aeration results in saturation of the water with nitrogen and oxygen and very good removal of other gases.

As equations (1), (2) and (3) show, the solution of the gases in water is a reversible reaction. To obtain almost complete removal of these gases by aeration, advantage may be taken of the common ion effect. That is, if the concentration of one of the ions on the right side of the equation is increased, the reaction is driven to the left, resulting in dissolution of the gas. In the case of carbon dioxide and hydrogen sulfide, hydrogen ion may be increased by adding an acid. Of course, any bicarbonate or carbonate in the water will be neutralized and the carbon dioxide formed will be removed by aeration.

In a similar manner, ammonia removal can be improved by increasing hydroxyl ion concentration through the addition of caustic soda.

Figures 3-2, 3-3, and 3-4 show percentage gas removal which may be obtained at the pH indicated.

The basic requirement for reducing gases by aeration is establishing a state of equilibrium between the gases in the water and those in the surrounding atmosphere. The removal of gases by aeration is favored by increase in temperature, increase in aeration time, increase in the volume of air in contact with the water and increase in the surface area of water exposed to the air. As indicated above, pH of the water is an important consideration. The efficiency of aeration is greater where the concentration of the gas to be removed is high in the water and low in the atmosphere.

Two general methods may be used to accomplish aeration of water. The most common in industrial use is forced draft aeration. Through the use of spray nozzles and packing or wood slat fill, the water is broken up into small droplets or a thin film to enhance countercurrent air contact.

The second method is to blow air into a receiver containing the water. Spargers or air diffusers are used to create very small air bubbles which insure good air-water contact for "scrubbing" the undesirable gas from the water.

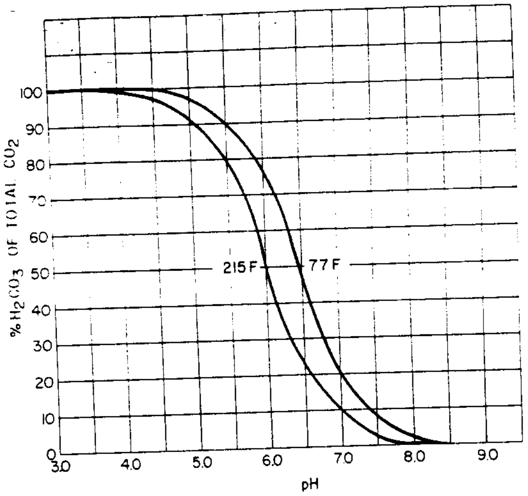

Figure 3-2. Percent CO_2 available for removal.

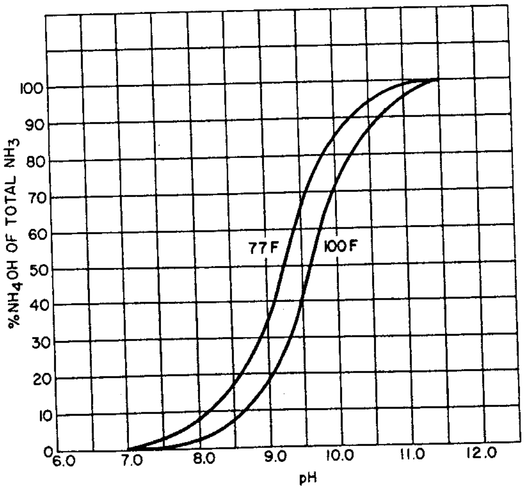

Figure 3-3. Percent NH_3 available for removal.

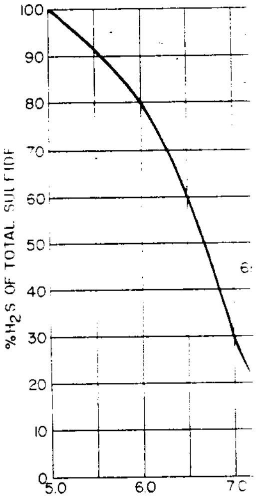

Figure 3-4. Percent H_2S av

WATER-FALL AERA

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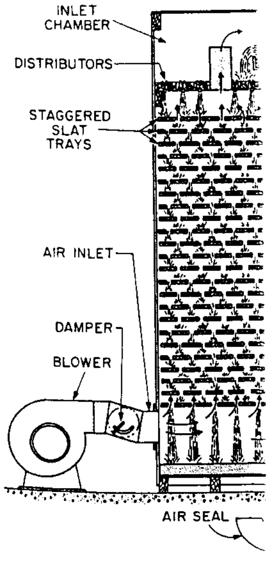
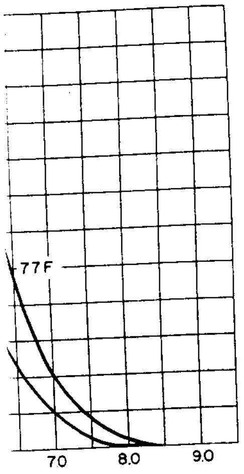


Courtesy of The Permutit Compan

Figure 3-5. Forced draft aer



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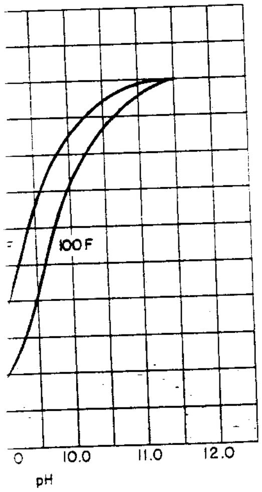

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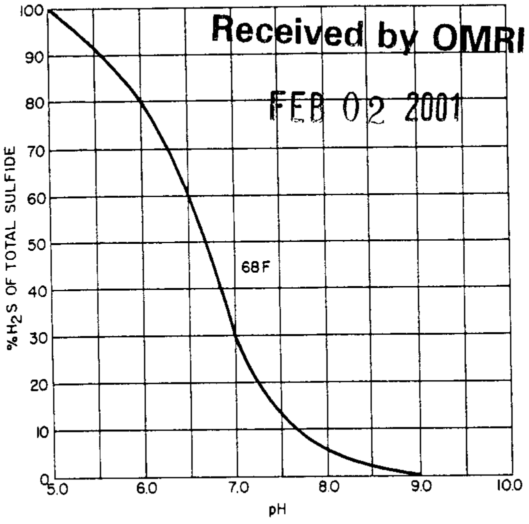
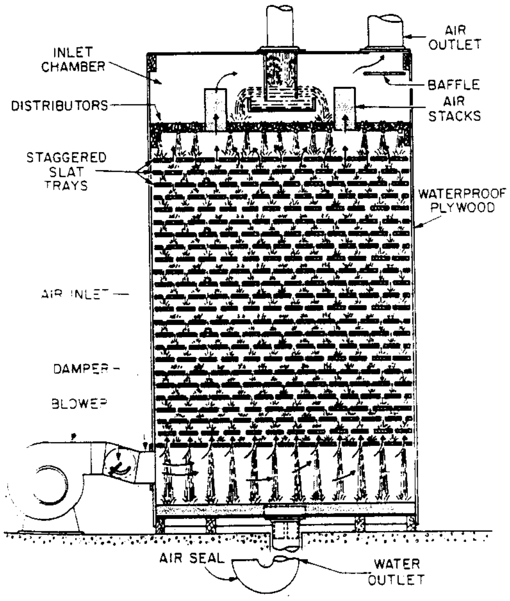


Figure 3-4. Percent H_2S available for removal.

WATER-FALL AERATORS

Many variations of the water-fall principle are used. The simplest is a vertical riser which discharges the water by free fall into a basin. The riser may operate on available head of water and the efficiency of aeration is increased by making the fall as great as practical. The addition of steps or shelves to break up the fall and to spread the water into thin sheets or films increases contact time and is a further refinement.



Courtesy of The Permutit Company, Inc.

Figure 3-5. Forced draft aerator.

Coke tray and wood slat aerators are relatively similar in design and have the advantage of smaller space requirements. Coke tray aerators are widely used in iron and manganese oxidation since a catalytic effect is secured by contact of the iron/manganese-bearing water with fresh precipitates. These units consist of a series of coke-filled trays through which the water percolates, with additional aeration obtained during the free fall from one tray to the next. Wood slat tray aerators are similar to small atmospheric cooling towers. The tray slats are staggered so as to break up the free fall of the water and create thin water films before it finally drops into the basin.

Forced draft aerators are more practical for many industrial water conditioning purposes. These units provide horizontal wood slat trays or packing which divide the falling water into small streams. Air is forced up through the unit by a blower with uniform air distribution across the entire cross-section. Air flow is countercurrent to the fall of the water and positive air circulation prevents any stagnant areas. Because of these features, forced draft aerators are more efficient for gas removal and require less space for a given capacity.

Air Diffusion. Air diffusion is accomplished by pumping air into water through perforated pipes, strainers, porous plates or tubes. Aeration by diffusion is theoretically superior to water-fall aeration since a fine bubble of air rising through water will continually be exposed to fresh liquid surfaces, providing maximum water surface per unit of air. Also, the velocity of bubbles ascending through the water is much slower than the velocity of free-falling drops of water, providing a longer contact time.

APPLICATIONS

In industrial water conditioning, one of the major applications of aeration is the reduction of corrosive gas concentration, such as carbon dioxide or hydrogen sulfide. On many occasions aeration is used to reduce the carbon dioxide liberated by a treatment process. For example, acid may be fed to the effluent of sodium zeolite softeners for boiler alkalinity control. Carbon dioxide is produced as a result of the acid treatment and aeration is employed to rid the water of this corrosive gas. Similarly, when the effluents of hydrogen and sodium zeolite units are blended, the carbon dioxide

Courtesy of Infilco Degremont, Inc.
Figure 3-6. Multicone aerator.

formed is reduced by aeration.

In the case of lime softening, carbon dioxide is removed before it can enter the equipment. Economics favor removal of high concentrations of carbon dioxide by aeration rather than by chemical precipitation with lime.

LIMITATIONS

Theoretically, at 68F it is possible to reduce carbon dioxide content of the water to 0.5 ppm by means of aeration to equilibrium conditions. Practically, it is not economical to attempt such complete gas removal and reduction of carbon dioxide to 10 ppm is normally considered satisfactory.

Although removal of free carbon dioxide increases the pH of the water and renders it less corrosive from this standpoint, aeration also results in the saturation of water with dissolved oxygen. In some cases, where the original oxygen content is already quite high, no undesirable effect is produced. However, in the case of a well supply high in carbon dioxide but devoid of oxygen, aeration may simply exchange one corrosive gas for another.

The efficiency of aeration is greatest when the initial concentration of the gas to be removed is considerably above its equilibrium value. Therefore, with waters containing only a small amount of carbon dioxide, neutralization by alkali addition is usually more cost effective.

Aeration alone will not secure the complete removal of hydrogen sulfide, but must be combined with pH reduction or chlorination.

Odors not due to gases of decomposition or to volatile oils will not be removed by aeration. Taste and odors due to industrial waste, phenols and creosols are unaffected by aeration. The medicinal taste imparted to water by chlorination of water containing phenols and creosols is also not removed by aeration.

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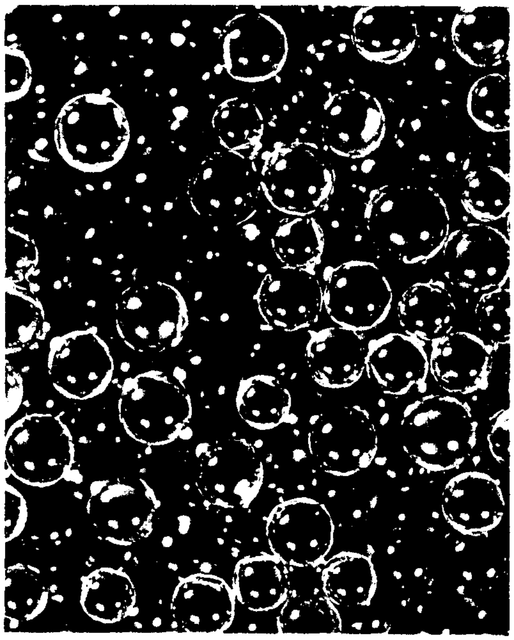
8 ion exchange

EVOLUTION

All natural waters contain, in varying concentrations, dissolved salts which dissociate in water to form charged particles called ions. The positively charged ions are called cations; the negatively charged ions, anions. Calcium, magnesium and sodium cations, along with bicarbonate, sulfate and chloride anions, are present in most raw water supplies. In ion exchange, ionic concentrations are expressed as ppm calcium carbonate; with the exceptions of carbon dioxide and silica, total cations exactly equal total anions.

Ion exchangers are materials that exchange one ion for another, hold it temporarily, and release it to a regenerant solution. These compounds are widely used to treat raw water supplies which contain dissolved salts. A proper regenerant can replace undesirable ions in the water supply with other more acceptable ions. For example, the commonly used sodium zeolite softener replaces scale-forming calcium and magnesium ions with sodium ions.



Courtesy of Rohm and Haas Company

Figure 8-1. Microscopic view of resin beads (20-50 mesh) of a sulfonated styrene divinylbenzene cation exchanger.

HISTORY

Two Englishmen, Thompson and Way, first investigated ion exchange in 1850, and reported that when a fertilizer solution passed through a column of soil, calcium replaced ammonia. In 1858, Eichman, a German chemist, discovered that the ion exchange process was reversible. Ion exchange was not used for any practical application, however, until 1905 when another German chemist, Gans, applied ion exchange to the softening (replacing calcium and magnesium ions with sodium ions) of water.

Gans water softeners used synthetic sodium aluminosilicate cation exchange materials called zeolites. The use of the Gans softening process spread widely, and because all ion exchange materials used during the first 30 years were either zeolites or materials resembling zeolites, the terms zeolite and sodium zeolite softener became firmly entrenched. Although zeolites (aluminosilicate) are rarely used today, the term zeolite softener is commonly used to describe any cation exchange process.

The synthetic zeolite exchange material which Gans used was soon replaced by a natural zeolite called Greensand. Greensand had a lower capacity than synthetic zeolite, but its greater physical stability made it more suitable for industrial applications. Capacity is defined as the amount of exchangeable ions a unit quantity of resin will remove from solution. It is usually expressed as kilograins per cubic foot as calcium carbonate.

The next major advance in ion exchange was in 1935 when sulfonated coal was developed as an ion exchanger. The sulfonated coal exchanger, commonly referred to as carbonaceous zeolite, extended the application of ion exchange to hydrogen cycle operation and provided a way to reduce alkalinity as well as

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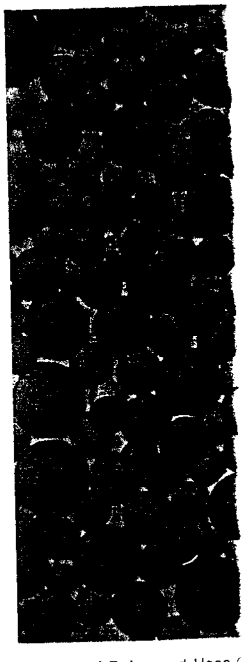

Courtesy of Rohm and Haas C

Figure 8-2. Microscopic
carboxylic exchanger res

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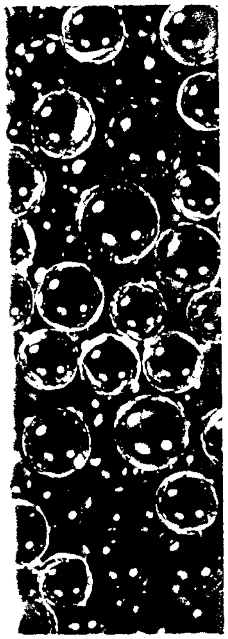

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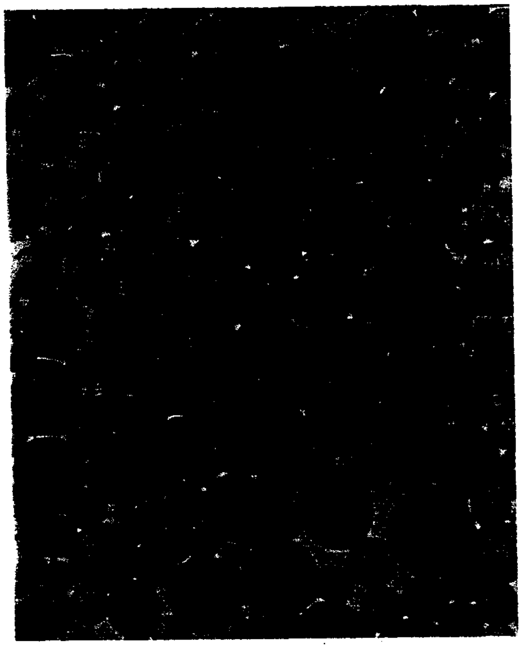
Soon after the introduction of carbonaceous zeolite, English chemists Adams and Holmes produced two new ion exchangers: a cation exchanger in the form of a phenolformaldehyde condensation product and an anion exchanger which was a condensation product of polyamines and formaldehyde. The advent of the anion exchanger led to the belief that complete demineralization (removal of all dissolved salts) of water would be possible, but early anion exchangers were unstable and could not remove such weakly ionized acids such as silicic or carbonic acid.

The 1944 research work of D'Alelio, an American, led to the development of cation exchangers produced by the copolymerization of styrene cross-linked with divinylbenzene. These resins were very stable and had several times the capacities of their predecessors. The polystyrene divinylbenzene anion exchanger, developed in 1948, can remove all anions, even weak acids such as silicic or carbonic. Further, these materials allow for the complete demineralization of water when preceded by a hydrogen cycle cation exchanger.

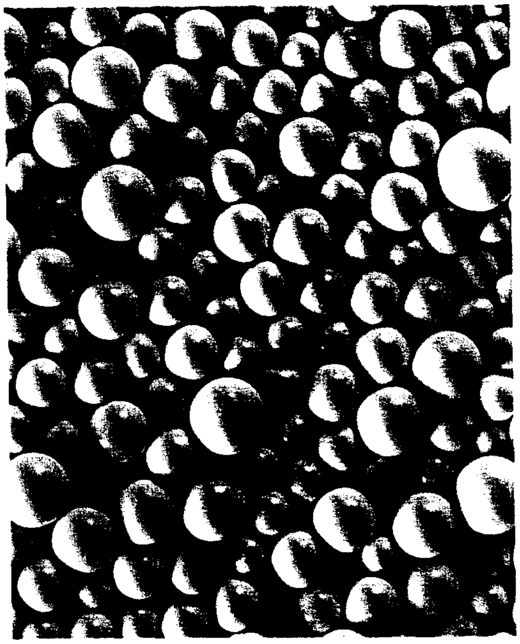
Since 1950, the original polystyrene divinylbenzene ion exchangers have been modified in many ways to meet the requirements of specific applications and to provide better resin life. Perhaps the most significant development has been the macroreticular (or macroporous) resin structure.

Unlike the gelular, permeable membrane structure of standard resins, all macroreticular resins have discrete pores and macroreticular cation resins possess a high resistance to thermal or osmotic degradation as well as oxidative attack. The macroreticular anion resins, due to their porous structure, are most resistant to organic fouling and are used ahead of the standard gelular resins to protect them from raw water organics.



Courtesy of Rohm and Haas Company

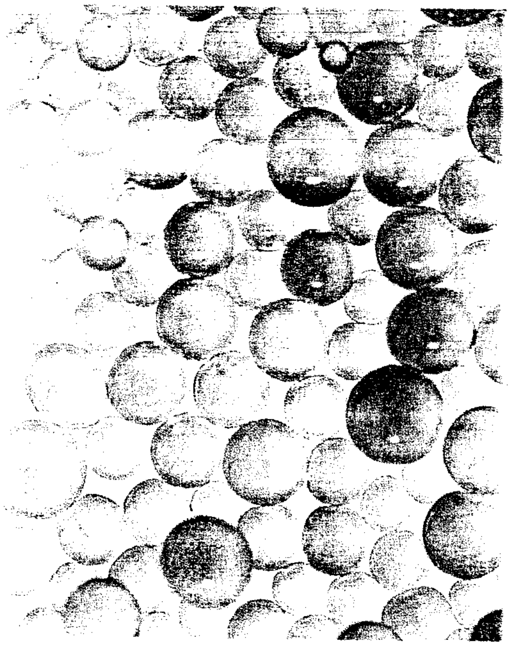
Figure 8-2. Microscopic view of beads (20-50 mesh) of carboxylic exchanger resin.



Courtesy of The Dow Chemical Company

Figure 8-3. Strong base anion resins.

Research and development by resin manufacturers and equipment vendors continue to improve present ion exchange processes and expand the areas of ion exchange application. Figure 8-1 shows a microscopic view of a typical sulfonated styrene divinylbenzene cation exchange resin. Figure 8-2 shows carboxylic-based resin beads. Figures 8-3 and 8-4 show corresponding strong and weak base anion resins. The large pore diameter (25,000 to 230,000 angstroms) of newer, highly porous anion exchange resins potentially may extend the scope of ion exchange applications to the removal of colloidal particles and large



Courtesy of The Dow Chemical Company

Figure 8-4. Weak base anion resins.

organic molecules.

Today's ion exchange resins consist of a hydrocarbon network to which ionizable functional groups are attached. The network may be formed from various organic materials, but the polystyrene divinylbenzene structure, developed in the 1940's, was so well suited to industrial water treatment that the majority of resins used today are of this structure. (See figure 8-5.)

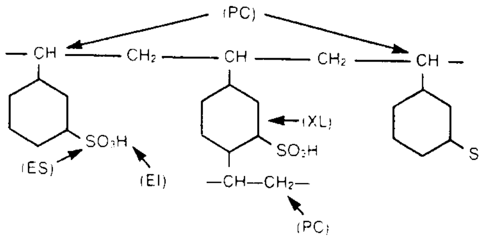
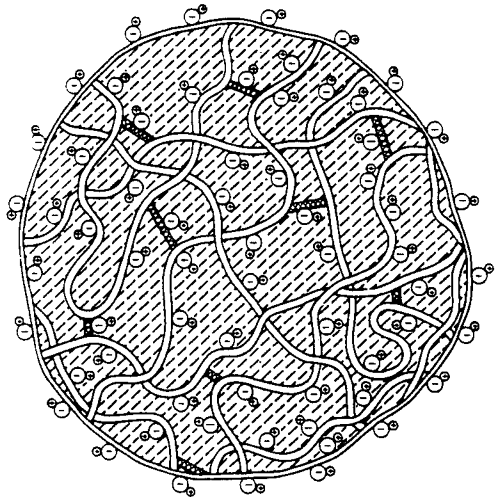


Figure 8-5. Chemical structural formula of sulfonic strong acid cation resin (Amberlite IR-120). (XL): crosslink; (PC): polymer chain; (ES): exchange site; (EI): exchangeable ion.

The ionizable groups within the beads give the resin the characteristics of a concentrated water solution in that they contain both positively charged cations and negatively charged anions. Unlike a water solution, however, only one ionic species is mobile; the other is attached to the bead structure. Figure 8-6 shows a schematic illustration of a strong cation exchange resin bead which has ion exchange sites consisting of immobile anionic (SO_3^-) radicals and mobile sodium cations (Na^+).



⊖ FIXED, NEGATIVELY CHARGED EXCHANGE SITE, e.g., SO_3^-

⊕ MOBILE, POSITIVELY CHARGED, EXCHANGEABLE CATION, e.g., Na^+

═ POLYSTYRENE CHAIN

XXXX DIVINYLBENZENE CROSS-LINK

▨ WATER OF HYDRATION

Courtesy of Rohm and Haas Company

Figure 8-6. Schematic of hydrated strong-acid cation exchanger.

Ion exchange occurs when raw water ions diffuse into the bead structure and the displaced ions from the bead structure diffuse back into the water solution.

CLASSIFICATIONS OF ION EXCHANGE RESINS

The ionizable group attached to the bead structure determines the functional capability of the resin. Present industrial water treatment resins may be classified as one of four basic types:

1. strong cation (SC),
2. weak cation (WC),
3. strong anion (SB), and
4. weak anion (WB).

The strong cation and the strong base anion resins can convert neutral salts into their corresponding acids and bases, respectively. This ability, called salt splitting, results in different

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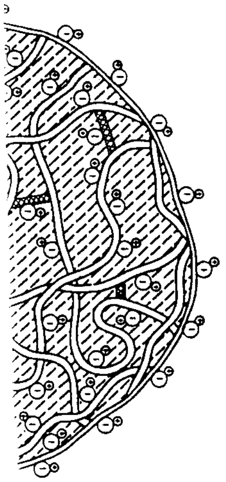

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SC resins derive their exchange activity from sulfonic acid functional groups (HSO_3^-). When operated on the hydrogen cycle they will remove nearly all raw water cations according to these reactions:

$$\begin{pmatrix}Ca\\Mg\\2Na\end{pmatrix}\cdot\begin{matrix}2HCO_3\\SO_4\\2Cl\end{matrix} + 2ZSO_3H = 2ZSO_3\begin{pmatrix}Ca\\Mg\\2Na\end{pmatrix}+\begin{pmatrix}2H_2CO_3\\H_2SO_4\\2HCl\end{pmatrix}$$

where Z represents the complex resin matrix. Because these reactions are reversible, when the resin capacity has been exhausted, it can be recovered through regeneration with a mineral acid.

Strong cation exchangers function well at all pH ranges and can split neutral salts into their corresponding acids. These resins have found a wide range of application, being used on the sodium cycle for softening and on the hydrogen cycle for softening and decationization.

Weak cation exchange resins have carboxylic groups ($-COOH$) as the exchange sites. When operated on the hydrogen cycle, WC resins can remove cations associated with alkalinity according to:

$$\begin{pmatrix}Ca\\Mg\\2Na\end{pmatrix}\cdot(HCO_3)_2 + 2ZCOOH =$$

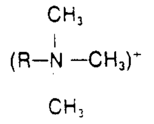
$$2ZCOO\cdot\begin{pmatrix}Ca\\Mg\\2Na\end{pmatrix} + 2H_2CO_3$$

These reactions are also reversible and permit acid regeneration to return the exhausted resin to the hydrogen form.

Because WC exchangers do not function efficiently at pH levels below 5.0, they cannot split neutral salts effectively. The main asset of the WC resins is their high regeneration efficiency which not only reduces the amount of acid required for regeneration, but also minimizes waste disposal problems.

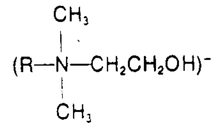
WC resins are used primarily for softening and dealkalization, frequently in conjunction with a strongly acidic polishing resin. Systems which use both resins profit from the regeneration economy of the weakly acidic resin while producing treated water of quality comparable to that available with a strongly acidic resin only.

Strong anion exchange resins derive their functionality from the quaternary ammonium exchange sites. Two species of quaternary ammonium exchange sites are commercially available and are commonly referred to as Type I and Type II. Type I sites have three methyl groups:



$$\left(R-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}-CH_3\right)^+$$

An ethanol group replaces one of the methyl groups in the Type II resin.



$$\left(R-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}-CH_2CH_2OH\right)^-$$

The principal difference between the two resins, operationally, is that Type I has a greater chemical stability, and Type II has a slightly greater regeneration efficiency and capacity.

In the hydroxide form, SB resin will remove all commonly encountered inorganic acids according to these reactions:

$$\begin{pmatrix}H_2SO_4\\2HCl\\2H_2SiO_3\\2H_2CO_3\end{pmatrix} + 2ZOH = 2Z\cdot\begin{pmatrix}SO_4\\2Cl\\2HSiO_3\\2HCO_3\end{pmatrix} + 2H_2O$$

Like the cation resin reactions, the anion exchange reactions are also reversible; regeneration with a strong alkali, such as caustic soda, will return the resin to the hydroxide form.

Weak anion resins derive their functionality from primary ($R\text{-}NH_2$), secondary ($R\text{-}NHR'$) and tertiary ($R\text{-}N\text{-}R_2$) amine groups. WB resin readily absorbs such free mineral acids as hydrochloric, sulfuric and nitric and the reactions may be represented as:

$$\begin{pmatrix}H_2SO_4\\2HCl\\2HNO_3\end{pmatrix} + 2ZOH = 2Z\cdot\begin{pmatrix}SO_4\\2Cl\\NO_3\end{pmatrix} + 2H_2O$$

WB resins are essentially mineral acid neutralizers. Because the above reactions are also reversible, WB resins can be regenerated by applying caustic soda, soda ash or ammonia. Regeneration efficiency of WB resins is substantially greater than for strong base resins.

While WB resins readily adsorb free mineral acids, these resins will not remove such weakly ionized acids as silicic and carbonic. Weakly basic resins are used in demineralizer systems in conjunction with strongly basic resins to reduce regenerant costs, to scavenge organics thereby protecting the more susceptible strongly basic resins, and for service in which carbon dioxide and silica are not important.

PART 1-SODIUM ZEOLITE SOFTENING

Sodium zeolite softening was the first industrial application of ion exchange and is the most common form involved in water conditioning. In this process, water passes through a bed of zeolite material which exchanges sodium ions for scale-forming ions of calcium and magnesium. The water so treated, called soft, is widely used for boiler feedwater, laundries and many types of chemical processes. As indicated previously, higher capacity resins have replaced zeolite materials in most applications, but systems using resins are still termed sodium zeolite softeners.

PRINCIPLES OF ZEOLITE SOFTENING

Sodium zeolite softeners use strong cation exchange resins of the polystyrene variety. The water to be softened passes through a column containing resin. The exchange of sodium ions for calcium and magnesium ions may be represented by:

$$\begin{pmatrix}Ca\\Mg\end{pmatrix}\cdot\begin{pmatrix}SO_4\\2Cl\\2HCO_3\end{pmatrix} + Na_2Z = Z\cdot\begin{pmatrix}Ca\\Mg\end{pmatrix} + \begin{pmatrix}2NaHCO_3\\Na_2SO_4\\2NaCl\end{pmatrix}$$

where Z represents the complex zeolite radical.

Although sodium zeolite-treated water is nearly free of all hardness constituents, some hardness leakage normally does occur. The amount of leakage depends primarily on the raw water hardness, sodium concentration and softener regeneration level.

Figure 8-7 represents an exhaustion profile which shows that the softener will produce a low, nearly constant effluent hardness until the ion exchange resin nears exhaustion. At this point, the hardness level usually will increase quite rapidly and resin regeneration will be required.

Regeneration is achieved by reversing the softening reactions. The exhausted resin is treated with a concentrated approximately [illegible] percent sodium chloride solution and regeneration proceeds according to this equation:

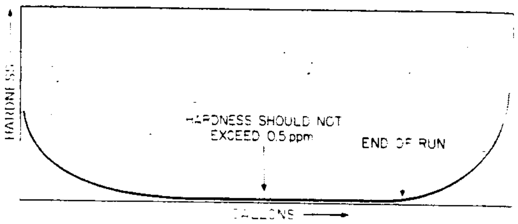


Figure 8-7. Sodium zeolite softener effluent

$$Z\cdot\begin{pmatrix}Ca\\Mg\end{pmatrix} + 2NaCl\ (concentrated) = Na_2Z + \begin{pmatrix}Ca\\Mg\end{pmatrix}\cdot Cl_2$$

Normally, zeolite more readily releases sodium in exchange for calcium and magnesium than the reverse. However, if excess sodium (the total amount of sodium in the brine exceeds the total amount of equivalent calcium and magnesium in the exhausted resin) is present in the brine and a considerable strength of brine (e.g., a 10 percent solution) is used for regeneration, the sodium cations can displace the previously removed calcium and magnesium cations much more readily. Thus, the salt solution concentration supplies the driving force for replacement of the hardness cations. The eluted hardness is then removed from the softening unit through the waste brine and rinse water streams.

The frequency of regeneration needed depends on the rate of softener flow, the calcium and magnesium content of the raw water, the quantity of exchange resin in the softener and the amount of salt used per regeneration. Of these, the operating plant usually controls only the quantity of salt used per regeneration. The other parameters are fixed by the system design and raw water hardness.

Figure 8-8, the capacity-salt level relationship for a standard polystyrene-eight percent divinylbenzene resin, shows the effect of regenerant level on softening capacity. Note that the capacity increases as the regenerant increases, but the change is not proportional. The higher the regenerant level, the less efficient the exchange. Therefore, softener operating costs increase when the regenerant level increases. The referenced data shows that a salt level of six pounds per cubic foot of resin produces a capacity of 18,000 grains per cubic foot, while a salt level of 15 pounds per cubic foot of resin

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produces a capacity of
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Salt pounds per cubic foot
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Figure 8-8. Effect of salt
polystyrene-eight percent
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SOFTENER OPERA

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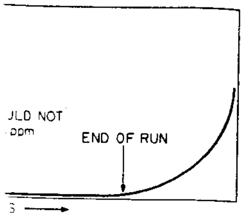

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produces a capacity of 30,000 grains per cubic foot. Thus, a 160 percent increase in salt usage, from 6 to 15 pounds per cubic foot, produces only a 50 percent increase in operating capacity.

Salt (pounds per cubic foot)	Capacity (grains per cubic foot)
6	18,000
8	20,000
10	24,000
15	30,000

Figure 8-8. Effect of salt level on capacity of standard polystyrene-eight percent divinylbenzene: operating, not laboratory, conditions.

SOFTENER OPERATION

A sodium zeolite softener operates through two basic cycles: the service cycle, which produces soft water for use, and the regeneration cycle, which restores the exhausted resin capacity.

During the service cycle, raw water enters the softener through the inlet distributor, flows through the resin bed, is collected by the underdrain system and is transferred to the point of use. The flow to the softener should be as constant as possible and sudden large surges or frequent on-off operation should be avoided.

The softening cycle is conducted most efficiently at a flow rate of approximately six to eight gpm per square foot of resin surface area, with all parallel units on-line. Equipment manufacturers generally design zeolite softeners for normal operation within this range, but provide for periodic runs at flow rates as high as 15 gpm per square foot. This allows total softened water requirements to be met while parallel units are regenerated.

Continuous operation at or above 15 gpm per square foot may result in channeling, bed compaction, leakage, or premature hardness breakthrough. Operation significantly below normal service flow rates (e.g., three gpm per square foot or less) can also produce difficulties such as decreased capacity and leakage. This potential exists because at low flow rates, water is not forced through the bed to insure optimum water-resin contact and complete exchange does not take place.

Some plants with dual softeners have found advantages in operating with one unit in standby. This approach eliminates the likelihood of both softeners needing regeneration at the same time, but a disadvantage does exist. Each time an idle softener is returned to service, it produces effluent of considerable hardness. This surge of hardness can be prevented by giving the softeners a short rinse prior to returning them to operation.

When a softener is exhausted it must be regenerated. A number of methods may be used to signal the need for regeneration. Some plants rely on operator testing while others regenerate after a fixed number of hours of softener operation. A common method for determining when a regeneration is needed is to measure the quantity of water treated between regenerations. A water meter in the service water line is used to either sound an alarm or automatically initiate regeneration when the preset number of gallons have been softened.

In recent years, many plants have installed automatic hardness titrators to control softener regenerations. These titrators assure the best quality water production because they provide continuous monitoring and are sensitive to changes in raw water composition, softener flow rates and regeneration efficiency. Regular maintenance is imperative to insure that the monitors are correctly functioning.

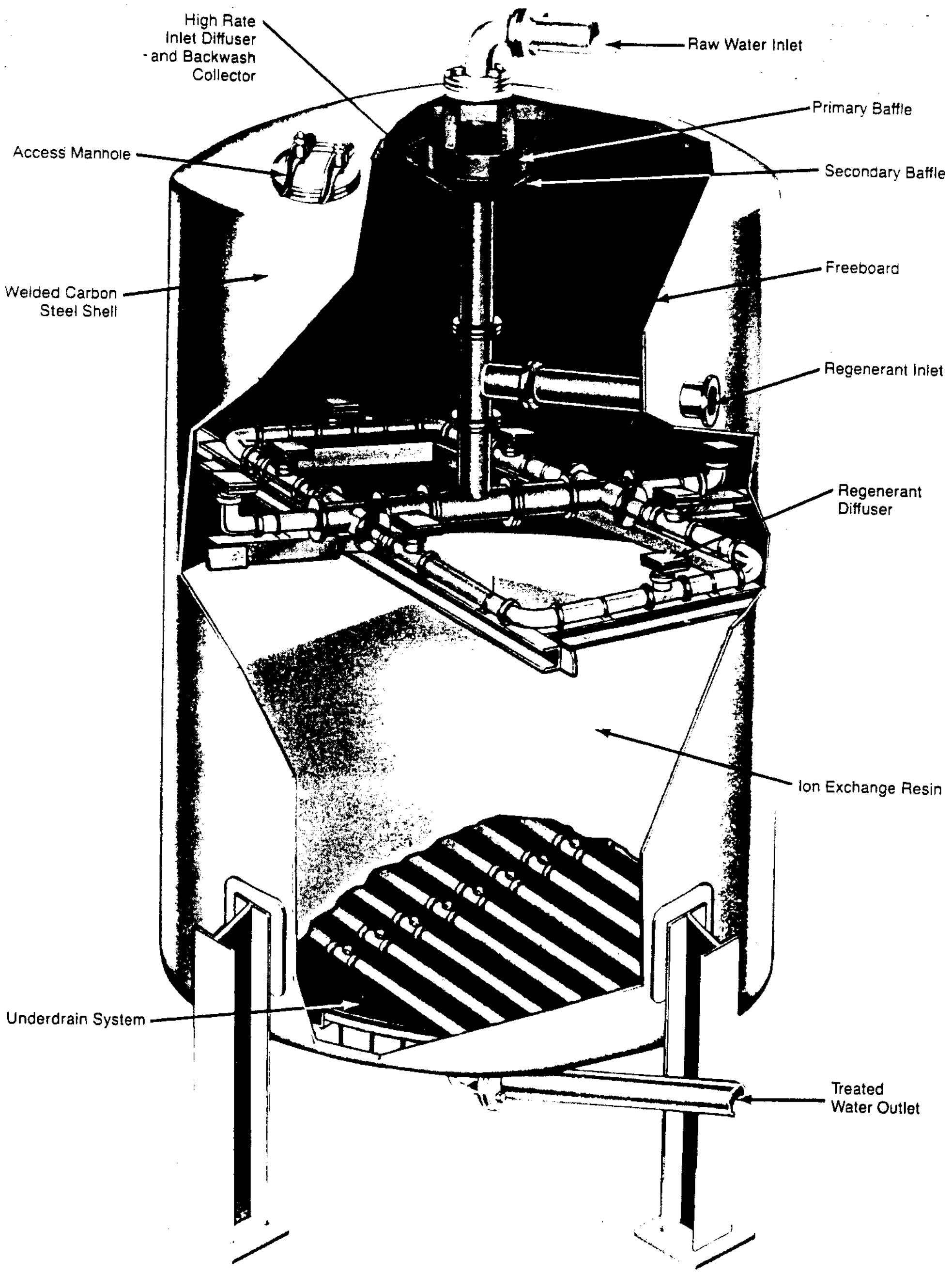
EQUIPMENT

Sodium zeolite softener systems consist of a softener tank, valving and a means for brining. Usually the softener tank is a steel, vertical-shell, pressure vessel with dished heads. The tank contains a service rinse water inlet distributor, free-board space, a regenerant distributor, a bed of ion exchange resin, supporting media or underdrain strainers or a header-lateral underdrain distribution system. A typical softening unit is shown in figure 8-9.

The service and rinse water inlet distributor, located in the top portion of the tank, consists of a baffle plate, or a hub and lateral system. Strainers and hoods are frequently incorporated as parts of the hub and lateral design, and special care is taken to avoid directing the water against tank walls which could cause channeling of the flow around the tank perimeter.

The inlet is designed to distribute the incoming water and prevents it from impinging on the resin bed and hollowing out cavities that would channel the flow, thereby reducing capacity and effluent quality. The distributor also acts as a collector for backwash water going to drain.

The free-board space (the volume between the top of the resin bed and the inlet distrib-



Courtesy of Graver Water Div., Ecodyne Corporation

Figure 8-9. Sodium zeolite softener.

utor) allows the resin to expand without loss to drain during backwashing and should be at least 75 percent of the resin bed volume.

The regenerant distributor, which is located about six inches above the resin bed, usually consists of a header lateral system and spreads the brine uniformly over the resin surface area. The location of the regenerant distributor prevents the water in the softener freeboard area from diluting the brine and reduces the time required for the flow or displacement rinse that follows brining.

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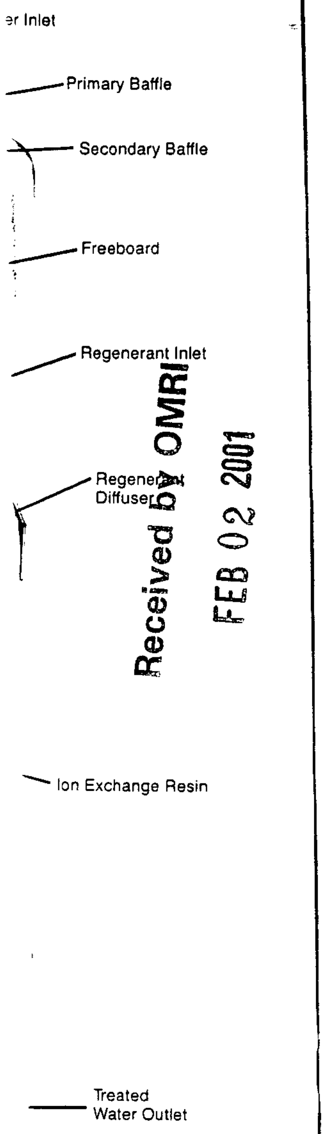

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The bed of strong cation resin, operating in the sodium cycle, softens the water. The quantity of resin used depends on the raw water hardness, the quantity of water to be treated per regeneration, and the regeneration level employed. A minimum bed depth of 24 inches is recommended for all systems.

The underdrain system, located in the bottom of the softener, includes the media or underdrain strainers which support the resin bed, collects the treated water, waste brine and rinse water and distributes backwash water. The underdrain system must collect water evenly from all portions of the bed during the service, brine and rinse operations. If the collection is not uniform, channeling may occur which will lower capacity and increase hardness leakage. Resin loss may occur either through carryover with the backwash water or as the result of an upset in the support material.

Although several different underdrain designs are used, there are primarily two distinctive types. The first is a header lateral collection system set in concrete with strainers protruding above the concrete base and layers of graded gravel or anthracite supporting the resin. The second is comprised of an internal, inverted dish, false bottom with strainers. The resin bed rests on the false bottom.

The valving system may consist of either a valve nest or a single multiport control valve. Six main valves exist: service inlet and outlet, backwash inlet and outlet, brine inlet and rinse outlet make up the valve nest needed to operate sodium zeolite softeners. The valves may be either manually operated gate valves or any variety of air, water or motor-operated automatic valves. A single multiport control valve may be used in place of the valve nest. As the multiport valve moves through a series of fixed positions, the ports in the valve direct the flow of water in the same manner as the opening and closing of six separate valves. Multiport valves, which are available for both manual and automatic regeneration systems, eliminate operational errors caused by opening or closing the wrong valves.

The brining system consists of separate salt-dissolving and brine-measuring tanks, or a combination salt-dissolving/brine-measuring tank. As its name implies, the salt-dissolving tank is used to prepare a saturated brine solution (approximately 26 percent NaCl). This tank frequently has a float-operated valve to control the fill and draw-down levels, and thus the quantity of brine added to the softener. Usually an eductor transfers the saturated brine to the softener, but a pump can be used. The inlet water to the eductor also dilutes the saturated brine to the desired concentration (approximately 10 percent) for resin regeneration. When a brine pump is used, an auxiliary line is needed to provide the dilution water.

SOFTENER REGENERATION

Softener regeneration consists of four steps:

Backwash. During the exhaustion or service cycles, the downward flow of raw water causes suspended matter to accumulate on the resin bed. The resin is an excellent filter medium. Backwashing is an upward flow of water which passes through the underdrain system, up through the resin bed, and out the service water distributor to waste. This reverse flow lifts and expands the resin bed by placing each bead in motion. In this manner, the bed is regraded while filtered particulates and resin fines are removed.

Regrading or classification of the zeolite resin brings the smaller beads to the top of the unit, larger beads go to the bottom. This enhances proper brine distribution. Expansion releases any material accumulated within the resin bed and fluffs the bed to allow for efficient brine-resin contact. Particulate matter and resin fines must be removed to prevent channeling, high pressure drop and poor kinetics.

Backwashing should be carried out for a minimum of 10 minutes or until the backwash water effluent is clear. The backwash water flow rate should be sufficient to produce a minimum of 50 percent bed expansion, yet not excessive enough to cause the loss of resin. The percent bed expansion resulting from a set flow rate is a function of the backwash water temperature; with a given flow rate, the lower the temperature, the more the bed is expanded. This is due to the increased viscosity of the water; therefore, adjustments in backwash water flow rates should be made as water temperatures vary seasonably. The optimum backwash flow rate will depend on the type of resin, water temperature and height of the free-board space. Backwash rates usually vary from 4 to 8 (ambient temperature) and 12 to 15 (hot service) gpm per square foot of tank area, but each manufacturer's recommendations should be carefully followed.

Brining. The brine regenerant stream enters the softener through the regenerant distributor, flows downward through the resin bed, is collected by the underdrain system and discharged to waste. The regenerant flow rate must be slow enough to provide sufficient brine-resin contact time, yet fast enough to prevent channeling of the brine. A normal 10 percent solution of brine should be added at a rate of approximately 0.5 to 1.0 gpm per cubic foot of resin in the softener to insure optimum contact time and regeneration efficiency.

Slow Rinse. A low flow of rinse water follows the regenerant to displace any remaining brine downward through the bed while slowly rinsing the unit. The rinse water enters through the regenerant distributor and should flow at the same rate as the brine in the previous step. The slow rinse completes regeneration by insuring that even the lowest portion of the resin bed is regenerated. This step insures proper regeneration.

The quantity of slow rinse water required is approximately one-half the resin bed volume plus the water volume from the resin surface to the regenerant laterals. This provides a "plug" of slow rinse water which forces the remaining brine completely through the bed.

Fast Rinse. A high flow of rinse water follows the slow rinse procedure to remove residual brine from the resin bed while eluting residual calcium and magnesium ions to waste. The fast rinse flow rate should be 1.5 gpm per cubic foot of resin.

At first, the rinse water will contain large quantities of calcium, magnesium and sodium chloride. The calcium and magnesium hardness will be rinsed from the softener before the sodium chloride. Usually a unit can return to service as soon as the hardness value reaches the desired pre-set level, but some operators continue the rinse until chlorides are reduced to a value near that of the influent level. A thorough fast rinse is quite important to insure effluent quality during the subsequent service run.

PART 2-HOT ZEOLITE SOFTENING

Before the development of polystyrene resins, it was common practice to use hot lime-soda or two stage hot lime-hot phosphate softeners to reduce boiler makeup alkalinity, hardness and silica. Since polystyrene resin may be used at temperatures up to 270F, it became a logical treatment way to remove residual hardness.

For maximum economy, lime alone is used in the first stage. Following filtration, the water is treated by zeolite softeners operating in the sodium cycle.

The softening equipment and operation are identical to that used for treating water at ambient temperature except that valves, controllers and meters must be suitable for high temperature (227-240F) operation. Also, during regeneration of the hot zeolite, a back pressure is maintained on the unit to prevent flashing of the water within the tank.

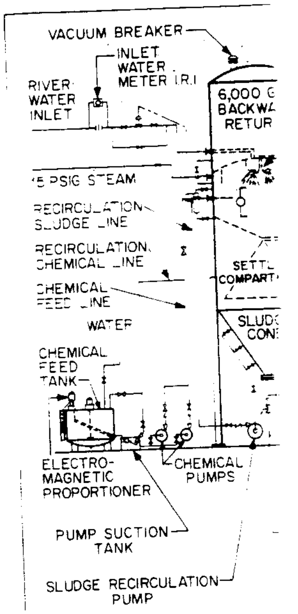
APPLICATIONS AND ADVANTAGES

The potential for scale and deposit build-up in boilers and the formation of insoluble soap curds in washing operations have created a large demand for softened water. The ability of the sodium zeolite softener to satisfy this demand economically has assured its use for preparing boiler feed, laundry and many types of chemical process waters. Compared to other softening methods, sodium zeolite units offer many advantages:

1. The treated water has a very low scaling tendency because this method reduces the hardness level of most water supplies to less than two ppm.
2. Operation is simple and reliable; automatic regeneration controls are available at reasonable cost.
3. Regeneration is accomplished with inexpensive, easy-to-handle salt.
4. Waste disposal usually presents no problem.
5. Within limits, variations in the water flow rate have little effect on treated water quality.
6. Efficient operation can be obtained in almost any size unit, making sodium zeolite softeners suitable for both large and small installations.

LIMITATIONS

While sodium zeolite softeners efficiently reduce the calcium and magnesium content of a raw water supply, they do not affect the alkalinity, silica or dissolved solids content. Plants which replace lime or lime/soda ash softeners with sodium zeolites have experienced very high boiler water alkalinity, silica and dissolved solids concentra



Courtesy of Water Conditioning D

Figure 8-10. Hot lime/hot ior

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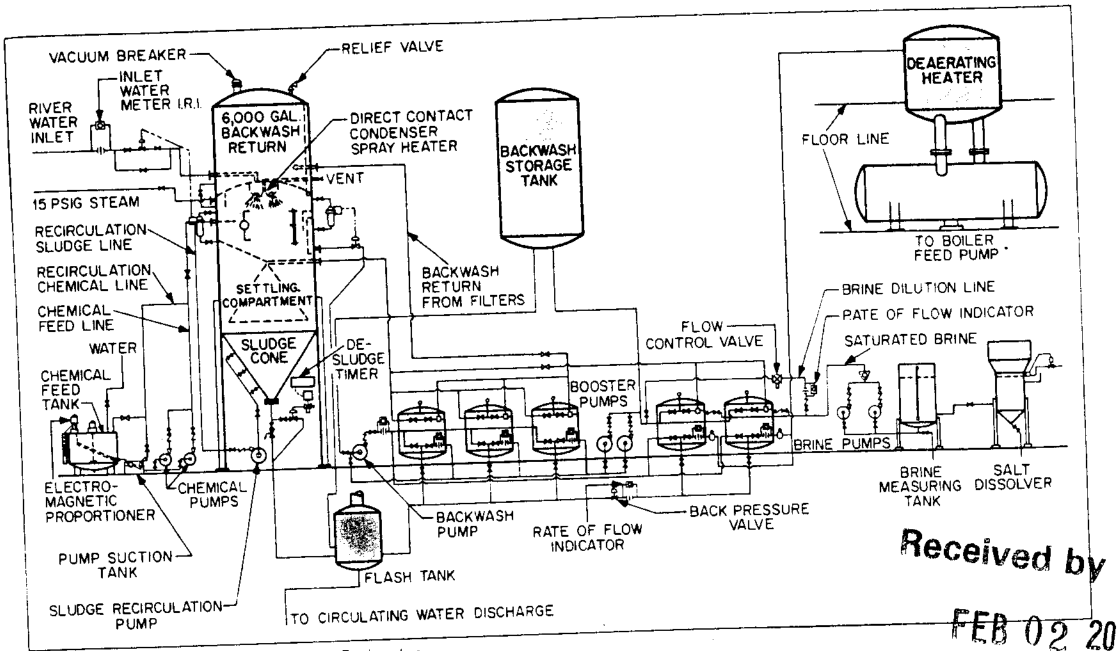

Courtesy of Water Conditioning Division, Envirex Inc.

Figure 8-10. Hot lime/hot ion exchange softening system.

Sodium zeolite softeners will not function efficiently on turbid waters. In general, if raw water turbidity exceeds 1.0 unit, it should be removed prior to softening. City and well water supplies are usually quite suitable for use, but surface waters often must be clarified and filtered.

Iron in the raw water supply can be detrimental to the ion exchange resin, and if it exceeds approximately 0.1 ppm, should be removed prior to softening. Whenever iron or other metallic contaminants are present, the softener must be backwashed thoroughly and a suitable resin cleaner applied during regeneration.

Aluminum-contaminated waters may also foul sodium zeolite ion exchange resins. Aluminum may be present in the raw water supply, but problems associated with it generally arise from the use of aluminum compounds for flocculation. Whenever aluminum coagulants are used ahead of sodium zeolite softeners, close pH control is essential to good softener performance.

Strong oxidizing agents in the raw water will attack ion exchange resin. Chlorine is a powerful oxidant, and if present, should be eliminated with a reducing agent such as sodium sulfite.

PART 3-SOFTENING AND DEALKALIZATION

Many waters must be softened and dealkalized before they are suitable for use, and several successful ion exchange processes have been developed to fill this need. The most prominent of these are: sodium zeolite/hydrogen zeolite split-stream softening, sodium zeolite/chloride anion dealkalization, and weakly acidic cation exchange.

SODIUM ZEOLITE/HYDROGEN ZEOLITE SPLIT-STREAM SOFTENING

The sodium zeolite/hydrogen zeolite split-stream softening system consists of one or more brine-regenerated sodium zeolite softeners and one or more hydrogen zeolite softeners. The same strong cation resin is used in both sodium and hydrogen units. Water passes through the sodium zeolite and hydrogen zeolite units in parallel, and the unit effluents are blended to produce water of a desired alkalinity.

The operation of the sodium zeolite softener was described earlier. The hydrogen zeolite softener removes calcium, magnesium and sodium ions from the water by exchanging them for hydrogen ions as shown in the following reactions:

$$\begin{pmatrix}Ca\\Mg\\2Na\end{pmatrix}\cdot\begin{pmatrix}SO_4\\2Cl\\2HCO_3\\2NO_3\end{pmatrix}+2HZ=2Z\cdot\begin{pmatrix}Ca\\Mg\\2Na\end{pmatrix}+\begin{pmatrix}H_2SO_4\\2HCl\\2H_2CO_3\\2HNO_3\end{pmatrix}$$

where Z represents the complex zeolite radical. The reactions show anions converted into their corresponding acids. The total concentration of the strong acids (H_2SO_4, HCl, HNO_3) produced is called the free mineral acidity or FMA, expressed as ppm. calcium carbonate.

During a typical hydrogen zeolite service cycle, free mineral acids are produced throughout the service run with only minor variations prior to exhaustion. The treated water is almost completely free of calcium and magnesium ions. The amount of sodium leakage depends primarily on the ratio of sodium to total cations, the ratio of alkalinity to total anions in the raw water, and the acid regenerant dosage. In general, the leakage increases as the raw water sodium concentration increases, and decreases as the raw water alkalinity and resin regenerant levels increase.

The concentration of the free mineral acidity drops sharply as a hydrogen zeolite column nears exhaustion. At this point the resin must be regenerated by treating it with an acid solution. Although other acids can be used, sulfuric is usually the preferred acid for economic reasons. Sulfuric acid, applied to the resin at a concentration range of two to six percent, regenerates the exchanger according to these reactions:

$$2Z\cdot\begin{pmatrix}Ca\\Mg\\2Na\end{pmatrix}+H_2SO_4=2HZ+\begin{pmatrix}CaSO_4\\MgSO_4\\Na_2SO_4\end{pmatrix}$$

The high acid concentration provides the driving force for displacing the calcium, magnesium and sodium ions, replacing them with hydrogen ions. As with the sodium zeolite softener, an excess of regenerant must be used, and while regeneration efficiency depends primarily on the resin regenerant level, usually two to three times the theoretical (stoichiometric) acid requirement must be used.

The water produced by the sodium and hydrogen zeolite columns is soft (low in calcium and magnesium). Sodium zeolite water contains a mixture of sodium salts, and the hydrogen zeolite water contains a mixture of acids. The sodium zeolite alkalinity ($NaHCO_3$) is used to neutralize the mineral acids in the hydrogen zeolite water according to these reactions:

$$2NaHCO_3+\begin{pmatrix}2HCl\\H_2SO_4\\2HNO_3\end{pmatrix}=\begin{pmatrix}2NaCl\\Na_2SO_4\\2NaNO_3\end{pmatrix}+2H_2CO_3$$

In addition to neutralizing the mineral acids, the above reactions convert the sodium alkalinity to carbonic acid (H_2CO_3) which, being very unstable in aqueous solutions, is easily removed by decarbonation in a forced draft decarbonator or vacuum degasifier.

The alkalinity of the treated water is maintained at the desired level by varying the percentages of sodium and hydrogen zeolite water in the blend. For a given water, the higher the sodium zeolite percentage, the greater the alkalinity; the higher the hydrogen zeolite percentage, the lower the alkalinity.

The approximate percentages of sodium and hydrogen zeolite water required for a blend can be predicted from these factors:

1. the alkalinity of the influent (Ai),
2. the free mineral acidity (FMA) of the hydrogen zeolite effluent, which depends on the sulfate, nitrate and chloride concentrations in the influent, and
3. the desired alkalinity in the mixed effluent (Am).

With the above information, the proper proportion can be calculated:

$$\text{Percent hydrogen zeolite}=\frac{Ai-Am}{Ai+FMA}\times 100$$

For example, given a water with:

Total Hardness as $CaCO_3$	36 ppm
Calcium as $CaCO_3$	24 ppm
Magnesium as $CaCO_3$	12 ppm
Methyl Orange Alkalinity as $CaCO_3$	34 ppm
Sulfate as SO_4	4 ppm
Nitrate as NO_3	2 ppm
Chloride as Cl	6 ppm
Carbon Dioxide as CO_2	15 ppm

Assume an alkalinity of 15 ppm as calcium carbonate is required in the blended effluent, given Ai of 34 ppm as $CaCO_3$, and the desired Am of 15 ppm as $CaCO_3$.

The FMA is the only additional value

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SO_4 = 4 × 1.0
NO_3 = 2 × 0.8
Cl = 6 × 1.4

Substituting in t

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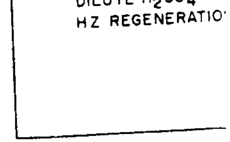

Figure 8-11. Hydrogen

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$$\begin{pmatrix}2NaCl\\ Na_2SO_4\\ 2NaNO_3\end{pmatrix} + 2H_2CO_3$$

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needed to apply the formula and calculate the percentage of water treated by the hydrogen zeolite unit. The FMA value is equal to the sum of the acids of the sulfates, nitrates and chlorides present in the water, but they must be converted to a common chemical equivalent so they can be added. The common basis chosen is $CaCO_3$. The constants used for these conversions are:

SO_4 – 1.04; NO_3 – 0.81; Cl – 1.41

Therefore, the FMA value can be calculated:

		ppm as $CaCO_3$
SO_4	= 4 × 1.04 =	4.2
NO_3	= 2 × 0.81 =	1.6
Cl	= 6 × 1.41 =	8.5
	FMA =	14.3

Substituting in the formula:

$$\text{Percent hydrogen zeolite} = \frac{34 - 15}{34 + 14.3} \times 100 = 39 \text{ percent}$$

Equipment. The hydrogen zeolite/sodium zeolite split-stream softening system consists of one or more hydrogen zeolite units, one or more sodium zeolite units, a decarbonator and a blending control system. Figure 8-11 is a flow diagram for a typical system.

Operation of sodium zeolite softeners was presented in detail earlier. The hydrogen zeolite softener also consists of a vertical-shell pressure vessel with distributors, underdrain and valving systems of the same design. The primary difference is that the hydrogen zeolite system uses materials suitable for acid service.

The hydrogen zeolite tank is lined with rubber or other suitable materials, and the fittings, valves and effluent piping are also rubber-lined or of other acid-resistant construction. Basically, this unit is similar to that shown in figure 8-9. The regenerant system is designed to handle sulfuric acid, and a number of arrangements are provided for preparing the two to six percent acid concentration needed for regeneration. The most effective method uses in-line blending of concentrated sulfuric acid with dilution water which flows at a constant rate. Concentrated sulfuric acid enters the dilution line through a suitable mixing tee and the flow of concentrated acid is regulated to provide the desired regenerant concentration.

The blending control, which proportions the sodium to hydrogen zeolite flow, is usually a simple rate-of-flow controller, but automatic analyzers can be used to compensate for changes in raw water characteristics to assure better control of the alkalinity of the treated water.

Decarbonators for removing carbon dioxide usually consist of wood towers or packed columns with forced draft fans. The blended effluent from the ion exchange columns is distributed over the top of the decarbonator, and wood slats or packing break the water into fine droplets or films. Air, introduced at the bottom of the decarbonator, flows counter-current to the falling water and scrubs it to provide a low carbon dioxide content in the effluent. Occasionally, vacuum degasifiers are used to remove carbon dioxide. A rubber-lined steel column is filled with packing to break the water into fine droplets and films, and steam jet ejectors, which apply a vacuum to

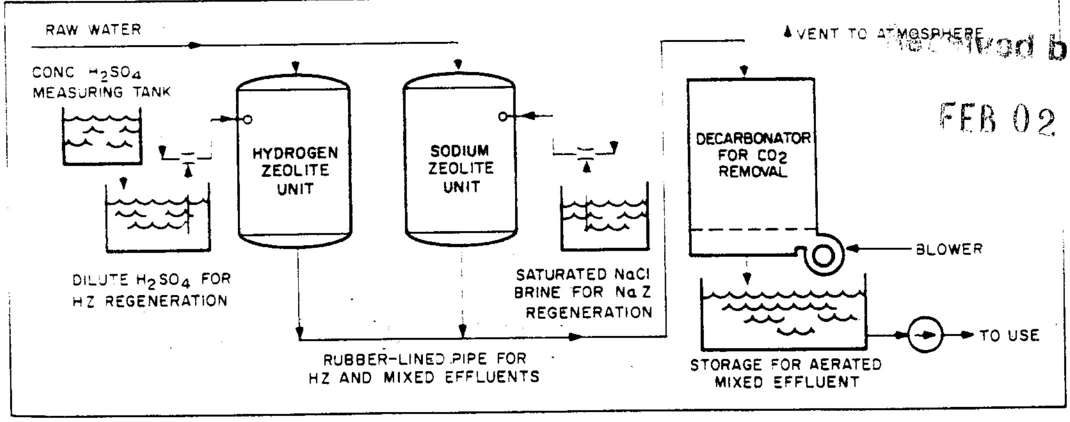

Figure 8-11. Hydrogen and sodium zeolite units in parallel.

the column, strip the dissolved gases from the water.

Operation. Hydrogen zeolite softener operation is very similar to sodium zeolite operation in that it uses the same basic service and regeneration cycles. Service water and regenerant flows follow identical paths with the same flow rate restrictions. The only major differences are the methods for determining the end of the service cycle and the use of sulfuric acid, rather than brine, as the regenerant.

A characteristic drop in free mineral acidity (FMA) occurs at the end of the hydrogen zeolite service cycle. This drop in FMA is frequently used to signal exhaustion and the need to regenerate the unit. This is usually 90 percent of the service cycle FMA. The drop in conductivity, which occurs when FMA is reduced, is also used for this purpose.

To compensate for changes in raw water characteristics, the ratio of the treated water conductivity to the conductivity of the water just above the bottom of the resin bed (anticipatory probe) may be used for signaling regeneration. During the service run, the two conductivities will be the same, but at the end of the run, the conductivity of the water above the bottom of the resin bed will drop before the final effluent conductivity is affected.

When regeneration is required, the unit should be backwashed in the manner described for sodium zeolite softeners, and sulfuric acid added to the resin bed as specified in the instructions provided by the equipment manufacturer. Usually, a two percent acid solution is added to the unit at a rate of about 0.5 to 1.0 gpm per cubic foot of resin. This phase of the operation should be followed carefully because high acid concentrations and low flow rates will allow calcium sulfate to precipitate in the resin bed. After the initial stages of acid introduction, the regenerant concentration may be increased to four and then six percent to improve regeneration efficiency and to reduce sodium leakage during the subsequent service cycle.

Following the sulfuric acid application, the hydrogen zeolite softener should be rinsed in the same way as the sodium zeolite softener. Common practice is to rinse the unit until the FMA is within 10 to 20 percent of the FMA during the preceding service run, but different practices may be developed to suit plant needs.

Treated water from the sodium and hydrogen zeolite units is blended to yield the desired alkalinity. For boiler feedwater, an alkalinity of about 15 ppm is usually preferred. The blending control will automatically proportion the sodium zeolite to hydrogen zeolite flow rates, but to protect the system from the damage of a blending control malfunction, a regular control testing program should be maintained. Also, a pH monitor and provision for caustic feed to the decarbonator sump should be included in the design.

SODIUM ZEOLITE/CHLORIDE ANION DEALKALIZATION

Sodium zeolite/chloride anion dealkalization systems have one or more sodium zeolite softeners and one or more chloride anion dealkalizers (strongly basic anion exchange resin columns which are regenerated with salt and caustic). Water first passes through the softener and then through the dealkalizer which replaces bicarbonate, sulfate and nitrate anions in the softened water with chloride ions as shown in these reactions:

$$\begin{pmatrix}Na_2SO_4\\2NaHCO_3\\2NaCO_3\end{pmatrix} + 2ZCl = 2NaCl + 2Z\cdot\begin{pmatrix}SO_4\\2HCO_3\\2NO_3\end{pmatrix}$$

Treatment by a chloride anion dealkalizer results in a 90 percent alkalinity reduction. When the resin column nears exhaustion, the treated water alkalinity increases rapidly, thus signaling the need for regeneration.

The dealkalizer is regenerated by reversing the service reactions in this fashion:

$$2Z\cdot\begin{pmatrix}SO_4\\2HCO_3\\2NO_3\end{pmatrix} + 2NaCl = 2ZCl + \begin{pmatrix}Na_2SO_4\\2NaHCO_3\\2NaNO_3\end{pmatrix}$$

As in other ion exchange systems, the brine concentration provides the driving force for reversing the reactions.

A sodium chloride brine regenerant, to which a small amount of caustic soda has been added, will produce a higher operating capacity and a more consistent effluent quality than regeneration with salt alone.

Equipment. The sodium zeolite/chloride anion dealkalizer system consists of one or more sodium zeolite softeners, and one or more chloride anion dealkalizers. As shown in figure 8-12, the equipment is arranged for series flow.

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nearly identical to that of the sodium zeolite softener; the major differences are the use of a strongly basic anion exchange resin in the dealkalizer and the provision for adding small amounts of caustic soda along with the salt brine during regeneration.

Operation. The chloride anion dealkalizer differs from the sodium zeolite softener only in the specific controls used. The service water and regenerant flows follow the same routes through the equipment. Service flow rates should usually be restricted to six to eight gpm per square foot of service area; backwash water requirements should usually be 2.5 to 4.5 gpm per square foot (backwash flow for the anion unit is less than that for the cation because the anion resin is less dense); and rinse rates, 1.5 gpm per cubic foot of resin. The total rinse water requirements are usually about 75 to 100 gallons per cubic foot of resin.

When caustic soda is applied to aid the regeneration efficiency, it should be added in proportion to the brine to produce a regenerant solution which contains approximately 1.0 percent caustic and 10 percent salt. Care should be taken to use only soft water for the dealkalizer regeneration. Hard water in the presence of caustic soda can precipitate calcium carbonate and/or magnesium hydroxide in the resin bed.

WEAK ACID CATION EXCHANGE

Another approach to softening and dealkalization uses weak acid (carboxylic) cation exchange resins. Water passes through a column containing this resin in the hydrogen form. Cations (calcium, magnesium and sodium) associated with alkalinity are exchanged for hydrogen ions, as shown by these reactions:

$$\begin{pmatrix} Ca \\ Mg \\ 2Na \end{pmatrix} 2HCO_3 + 2HZ = 2Z \begin{pmatrix} Ca \\ Mg \\ 2Na \end{pmatrix} + 2H_2CO_3$$

where Z represents the resin complex. Decarbonation removes the carbonic acid (H_2CO_3) formed as it does in the sodium zeolite hydrogen zeolite split-stream system.

Raw water characteristics determine the final treatment water quality. In contrast with the hydrogen zeolite unit which uses a strongly acidic cation resin, the weakly acidic cation resin produces FMA during the first 40 to 60 percent of the exhaustion cycle. Because the raw cations associated with the sulfate, chloride and nitrate anions usually pass unaffected through the weak acid resin column, the treated water will contain hardness, if the raw water hardness exceeds the alkalinity. For example, raw water hardness and alkalinity levels of 150 and 100 ppm, respectively, produce a treated water hardness level of nearly 50 ppm. Consequently, the weakly acidic resin column may need to be followed by a sodium zeolite softener to remove the remaining hardness. However, the optimum hardness to alkalinity ratio (A/M) of a water to be treated by this process is 1.0.

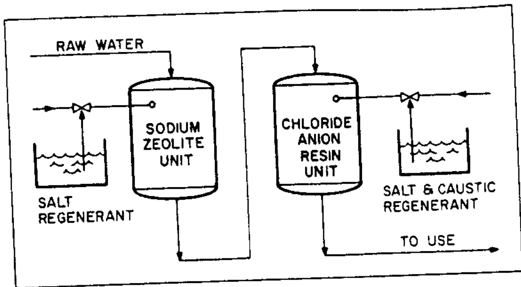

Figure 8-12. Sodium zeolite-chloride anion exchanger.

The regeneration frequency of a weak acid cation exchange resin column is usually determined by the treated water hardness or alkalinity level. Regeneration, accomplished by treating the resin bed with a 0.5 to 0.7 percent sulfuric acid solution, proceeds as illustrated in these reactions:

$$2Z \cdot \begin{pmatrix} Ca \\ Mg \\ 2Na \end{pmatrix} + H_2SO_4 = 2HZ + \begin{pmatrix} CaSO_4 \\ MgSO_4 \\ Na_2SO_4 \end{pmatrix}$$

Since the regeneration efficiency of these resins approaches 90 percent, only slightly more than the theoretical quantity of acid is required to regenerate these columns. By comparison, most strong acid cation exchangers have regeneration efficiencies of 30 to 40 percent, thereby requiring 2.5 to 3.0 times the amount of acid regeneration.

Equipment. The weak acid cation exchange unit is identical to the standard hydrogen zeolite unit. The difference in performance is the result of using the weak acid resin. The unit is followed by a sodium zeolite softener and a decarbonator. Another arrangement includes a layer of strong acid cation resin beneath the weak acid resin, rather than a separate sodium zeolite softener. Provisions for applying a salt wash after the acid injection are included.

Operation. The operation of the weak acid cation exchanger is similar to that of the sodium zeolite and hydrogen zeolite softeners, differing only in the specific controls used. Service water flow rates can significantly affect operating capacity and should be limited to six to eight gpm per sq. ft. Backwash flow rates of about four to six gpm per sq. ft. of surface area are considered normal, and the rinse water requirement is about 75 gallons per cubic foot of resin.

Sulfuric acid is normally used for regeneration, but because the weak acid resin has a great affinity for calcium, the resin is more susceptible to calcium sulfate precipitation than the strong acid resin used in the typical hydrogen zeolite unit. To avoid precipitating calcium sulfate, the sulfuric acid concentration should not exceed 0.7 percent.

Strong acid cation resin may be used with the weak acid resin to achieve softening and dealkalization. The strong acid resin, because of density difference, will be on the bottom of the resin column following backwash. After acid addition, a 10 percent solution of salt, sodium chloride, is passed through the bed. The salt serves to exhaust the strong acid sites on the weak acid resin and regenerate the strong cation resin into the sodium form. This does not affect the weak acid resin's capacity because it exchanges cations associated with alkalinity. As noted above, without salt treatment, there will be FMA in the weak acid effluent for the first 40 to 60 percent of the run.

OTHER PROCESSES

Other ion exchange processes are also used to soften and dealkalize water. Sodium zeolite softening, followed by the direct feeding of sulfuric acid and decarbonation, is one approach. The sulfuric acid converts the softened water bicarbonate into carbonic acid and sodium sulfate; the carbonic acid is then removed in the decarbonator as carbon dioxide. However, the use of this method should be approached with caution to prevent low pH feedwater resulting from acid overfeed. Provision for pH monitoring and caustic backfeed should be included.

APPLICATIONS AND ADVANTAGES

The sodium zeolite/hydrogen zeolite split-stream process produces a low hardness, low alkalinity water and reduces the dissolved solids content of the water in direct proportion to the alkalinity reduction achieved. This process is quite suitable for producing boiler feedwater for small to medium-sized systems and process water for the carbonated beverage industry.

The sodium zeolite/chloride anion dealkalizer system produces a water low in hardness and low to moderate in alkalinity. Alkalinity is reduced without the hazard of handling acid, and although caustic soda used with salt regenerant improves the operating capacity, salt alone may be used. This process is primarily used to produce boiler feedwater for small plants.

Weak acid cation exchange produces water of a quality comparable to that produced by the sodium zeolite/hydrogen zeolite split-stream system. Excellent hardness and alkalinity reduction can be achieved with a corresponding reduction in the dissolved solids content. Because the weak acid resin has a high regeneration efficiency, it offers substantial economic advantage. This system can usually be installed wherever sodium zeolite/hydrogen zeolite split-stream softening systems have been used, but system selection must be based on specific plant needs.

LIMITATIONS

The softening and dealkalizing processes, like other ion exchange systems, will function efficiently only if the raw water contains no suspended matter. Iron and aluminum in the raw water supply can foul sodium zeolite softeners, and under certain circumstances, can also foul acid-regenerated ion exchangers. Chlorine or other oxidizing agents in the water supply will attack the ion exchange resins and significantly reduce their useful life.

The softening and dealkalization processes do not reduce the raw water silica content; split-stream and weak acid cation exchange systems decrease dissolved solids to a limited extent, but chloride anion dealkalization does not significantly affect dissolved solids. The water produced by systems using forced draft decarbonators becomes saturated with oxygen, and consequently is highly corrosive.

PART 4-DEMINERALIZATION

Demineralization, as applied to water treatment, is the removal of essentially all inorganic salts by ion exchange. In this process, hydrogen cation exchange converts dissolved salts to

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their corresponding acids, and basic anion exchange removes these acids. The only other commercial process which produces water of comparable purity is distillation. Because demineralization of most fresh water supplies is substantially less expensive than distillation, it is widely used.

PRINCIPLES OF DEMINERALIZATION

The demineralizer system consists of one or more ion exchange resin columns, which includes a strong cation unit and a strong anion unit. The cation resin exchanges hydrogen for raw water cations as shown by these reactions:

$$\left(\begin{matrix}\mathrm{Ca}\\ \mathrm{Mg}\\ 2\mathrm{Na}\end{matrix}\right)\cdot\left(\begin{matrix}\mathrm{SO_4}\\ 2\mathrm{Cl}\\ 2\mathrm{HCO_3}\\ 2\mathrm{NO_3}\end{matrix}\right) + 2\mathrm{HZ} = 2\mathrm{Z}\cdot\left(\begin{matrix}\mathrm{Ca}\\ \mathrm{Mg}\\ 2\mathrm{Na}\end{matrix}\right) + \left(\begin{matrix}\mathrm{H_2SO_4}\\ 2\mathrm{HCl}\\ 2\mathrm{H_2CO_3}\\ 2\mathrm{HNO_3}\end{matrix}\right)$$

where Z represents the cation exchange resin complex.

The anion resin exchanges hydroxyl anions for the highly ionized anions as shown by these reactions:

$$\left(\begin{matrix}\mathrm{H_2SO_4}\\ 2\mathrm{HCl}\\ 2\mathrm{HNO_3}\end{matrix}\right) + 2\mathrm{ZOH} = 2\mathrm{Z}\cdot\left(\begin{matrix}\mathrm{SO_4}\\ 2\mathrm{Cl}\\ 2\mathrm{NO_3}\end{matrix}\right) + 2\mathrm{H_2O}$$

where Z represents the anion exchange resin complex.

Because the anion used in a demineralizer resin is strongly basic, it will also remove weakly ionized carbonic and silicic acids, according to these reactions:

$$\left(\begin{matrix}\mathrm{H_2CO_3}\\ \mathrm{H_2SiO_3}\end{matrix}\right) + \mathrm{ZOH} = \mathrm{Z}\cdot\left(\begin{matrix}\mathrm{HCO_3}\\ \mathrm{HSiO_3}\end{matrix}\right) + \mathrm{H_2O}$$

The above reactions indicate complete removal of cations and anions from the water, but in reality, these are equilibrium reactions, and even with very efficient column operation, leakage will occur. The leakage will vary according to the demineralizer system used, and for any given system, according to the raw water mineral composition and demineralizer regenerant level (the amount of acid and caustic used for regeneration). To minimize cation leakage, the exchanger may be regenerated upflow and operated downflow in the service cycle. This insures that the water will pass through the most highly regenerated resin just before leaving the unit.

Demineralizers which must remove silica use strong base anion resins, and both the silica content and specific conductance are important water quality criteria. Both values are high after regeneration and low after rinsing to produce satisfactory water quality. The silica level, nearly constant during the entire service run, increases sharply at the end; conductivity, also nearly constant during the service run, drops briefly at the end and then rises.

The temporary drop in conductivity when the resin capacity is first exceeded is easily explained. During the normal service cycle, a small amount of sodium leaks from the cation resin. As the anion resin is converting the anions to hydroxyl (OH^-) ions, sodium ions combine with these hydroxyl groups to produce small amounts of sodium hydroxide (NaOH) which is highly conductive.

When the capacity of the anion resin is exhausted, silica leakage converts the sodium leakage to sodium silicate, a material less conductive than sodium hydroxide. When a silica increase is detected, the demineralizer must be removed promptly from service. If the demineralizer is allowed to remain in service until the conductivity increases, not only will raw water silica leak through, but raw water sulfate and chloride ions will displace additional silica from the resin. Under these circumstances, the treated water silica can substantially exceed the influent raw water silica level.

Demineralization systems for producing water of extremely high purity use mixed bed demineralizers (an intimate mixture of strongly acidic cation and strongly basic anion resins in the same column). A typical mixed bed demineralizer will rinse down to low conductivity and silica values after regeneration. These values will remain low and nearly constant during the service cycle, but when the resin is exhausted, both values will increase concurrently.

Treated water quality will decrease when resin capacity is exceeded, thus indicating the need to remove the unit from service for regeneration. The cation exchange resin is regenerated with acid as described for a hydrogen zeolite unit. The anion exchange resin is regenerated with an alkaline material. Caustic soda is the most common regenerant. Caustic soda, usually applied as a four percent solution, regenerates the resin in accordance with these reactions:

$$2Z\begin{pmatrix}SO_4\\2Cl\\2NO_3\\2HCO_3\\2HSiO_3\end{pmatrix} + 2NaOH = 2ZOH + \begin{pmatrix}Na_2SO_4\\2NaCl\\2NaNO_3\\2NaHCO_3\\2NaHSiO_3\end{pmatrix}$$

The relatively high concentration of caustic soda provides the driving force necessary to reverse the service cycle reactions and regenerate the resin. Caustic soda is the preferred regenerant whenever silica must be removed. Weak base anion exchange resins may be regenerated with caustic soda, ammonia or soda ash.

Demineralizers which are employed where silica removal is not critical use weak base anion resins, and specific conductance is the primary parameter for evaluating water quality. Conductivity will remain at a low, nearly constant level during the entire service run and increase only when the resin capacity is diminished, thus allowing increased unit leakage.

Equipment. The demineralization system will vary according to the requirements of the application. Figure 8-13 shows nine basic demineralizer systems and lists areas of application, typical treated water quality and the relative advantages/disadvantages of each.

The cation and anion exchange columns for demineralization are similar to those described for hydrogen zeolite softening. The only difference is the use of anion resin in the anion exchange column. The piping, valves and fittings are made of lined or acid-resistant materials. When required, the decarbonator or vacuum degasifier is identical in design to the unit used in split-stream softening.

The mixed bed demineralizer is also similar to the hydrogen zeolite softener, except that the resin bed is a mixture of cation and anion exchange resins. In addition, sight glass windows and an interface regenerant collector are typically part of the design. One of the sight glass windows is located for observing the resin level in the unit since the loss of even small quantities of resin may cause poor performance. The lower sight glass window is positioned to allow detection of the line of separation between the cation and anion resins when the unit is prepared for regeneration. (See figure 8-14.)

Efficient regeneration requires a clear and distinct line of separation. If the resins are not completely separated, the anion resin that remains in the bottom of the unit will be regenerated with sulfuric acid which converts it to the sulfate form. Any cation resin in the upper portion of the column will be regenerated with caustic soda and converted to the sodium or exhausted form. Therefore, the operating capacity and treated water quality will both suffer if complete resin separation is not achieved prior to regeneration.

The interface regenerant collector, as its name implies, is positioned at the interface between the cation and anion resins to collect spent regenerant. If the unit does not contain the correct amount of cation resin, the regenerant collector will not be positioned properly with respect to the resin interface. The result will be similar to the effect of inadequate separation of the resins (a portion of the cation or anion resin will be treated with the wrong regenerant solution).

The mixed bed demineralizer is equipped for air injection into the bottom of the unit to re-mix the separated resins following regeneration. Both the quality of the treated water and the capacity of the unit may be affected if the resin is not thoroughly and uniformly mixed.

DEMINERALIZER OPERATION

Demineralizers operate much like other ion exchange systems. The cation exchange resin columns operate in the same manner as hydrogen zeolite softeners. The anion exchange resin columns follow the same basic service and regeneration cycles with the only differences being the use of an alkaline regenerant and a change in the specific controls.

The service flow rate should be restricted to the range of six to eight gpm per square foot of resin surface area during normal service and the effluent quality should remain nearly constant during the service run. At the end of a service run, the treated water conductivity and silica measurement determine the need for regeneration.

At the end of a strong base anion unit service run, silica will increase, pH will decrease and conductivity will temporarily decrease followed by an increase. A meter which measures the quantity of water treated, a continuous silica analyzer, and a conductivity probe located slightly above the bottom of the resin bed, may

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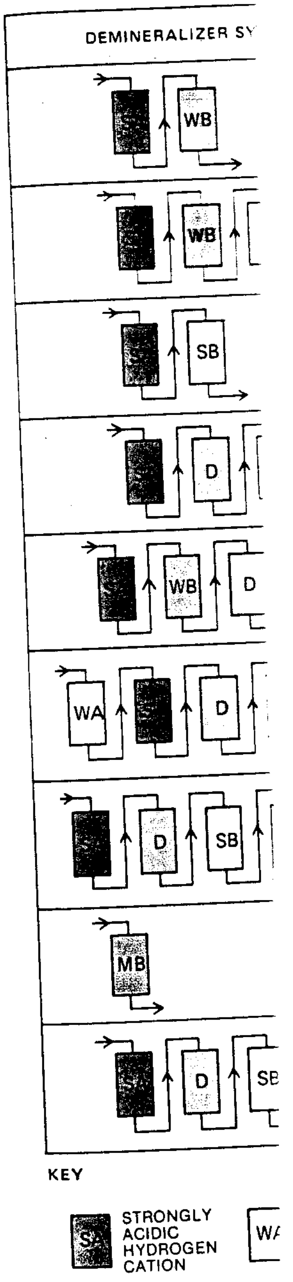

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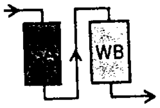
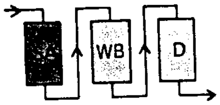
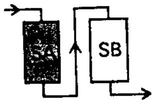
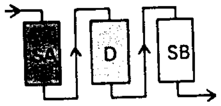
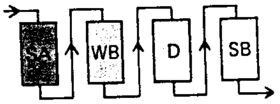
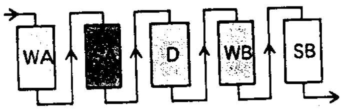
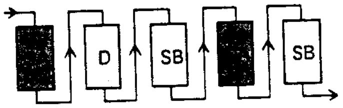
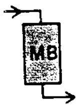
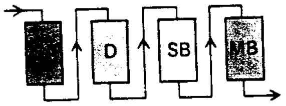
DEMINERALIZER SYSTEM	APPLICATION	TYPICAL EFFLUENT	ADVANTAGES AND DISADVANTAGES
	Silica and CO_2 are not objectionable.	Specific conductance 10-30 micromhos, Silica unchanged.	Low equipment and regenerant costs.
	Silica is not objectionable but CO_2 removal is required.	Specific conductance 10-20 micromhos, Silica unchanged.	Low regenerant costs, but requires repumping.
	Low alkalinity raw water, silica removal required.	Specific conductance 5-15 micromhos, Silica 0.02 to 0.10 ppm.	Low equipment costs, repumping not required, high chemical costs.
	High alkalinity, raw water, silica removal required.	Specific conductance 5-15 micromhos, Silica 0.02 to 0.10 ppm.	Low chemical costs, repumping is required.
	High alkalinity, sulfate and chloride raw water. Silica removal required.	Specific conductance 5-15 micromhos, Silica 0.02 to 0.10 ppm.	Low chemical costs, high equipment costs, repumping required.
	High hardness, alkalinity, sulfate and chloride raw water. Silica removal required.	Specific conductance 5-15 micromhos, Silica 0.02 to 0.10 ppm.	Lowest chemical cost, high equipment cost, repumping required.
	High alkalinity, high sodium raw water, high purity treated water required.	Specific conductance 1-5 micromhos, Silica 0.01 to 0.05 ppm	Low chemical costs, high equipment costs, repumping required.
	Low solids, raw water, high purity treated water required.	Specific conductance is less than 1 micromho Silica 0.01 to 0.05 ppm	Low equipment cost, high chemical cost.
	High alkalinity and dissolved solids raw water, high purity treated water required.	Specific conductance is less than 1 micromho Silica 0.01 to 0.05 ppm.	Lower chemical cost, higher equipment cost, requires repumping.

KEY

■ STRONGLY ACIDIC HYDROGEN CATION	WA WEAKLY ACIDIC HYDROGEN CATION	WB WEAK BASE ANION	SB STRONG BASE ANION	D DECARBONATOR OR VACUUM DEAERATOR	MB MIXED BED

Figure 8-13. Demineralizer systems.

be used to signal the need for regeneration.

Anion resin backwash water requirements will vary from one to three gpm per square foot of resin surface, depending on water temperature. Regenerant and rinse flow rates of 0.25 to 1.0 and 1.5 gpm per cubic foot of resin, respectively, are usually recommended. Hydrogen zeolite-treated water should be used for anion resin regeneration since untreated water will cause precipitation of calcium and magnesium salts on the resin bed.

The caustic soda, used to regenerate strong base anion resins, should be added to the unit as a four percent solution. Where silica must be removed, applying the regenerant at a temperature of approximately 120F will improve the regeneration efficiency. For optimum results, caustic addition should follow a preheat cycle during which warm water is passed through the resin bed to increase its temperature to

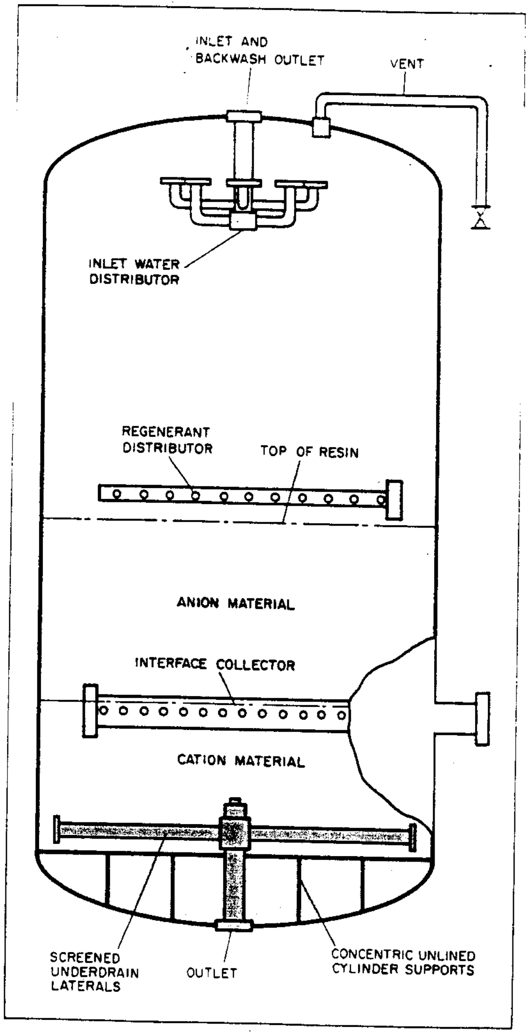


Figure 8-14. Mixed bed ion exchange unit, showing internal distributors.

approximately 120F.

Weak base resins can be regenerated with caustic soda, but less expensive materials, such as ammonia and soda ash, may also be used. Some weak base resins develop extended rinsing requirements when regenerated with caustic soda; ammonia regeneration has been successful in alleviating this problem.

A mixed bed demineralizer operates in a manner quite similar to the operation of other ion exchange systems. Effluent silica and conductivity remain at low, constant levels until the end of the service run, then both values increase. Conductivity measurements usually determine the point where regeneration is required. Resins must first be separated in a mixed bed demineralizer system before regeneration can start.

The resins in the mixed bed unit are regenerated within the operating column. Normal backwashing separates the resins by causing the less dense anion exchange resin to rise to the top. When the resin has settled after the backwashing, a distinct line, which is visible in the sight glass, should mark the separation of the cation and anion resin layers. If the two resins do not separate during the backwash cycle, backwashing should be continued until the distinct separation does occur and is clearly visible.

Once the resins have been separated, they can be regenerated by acid and caustic treatment in the normal manner. The acid, introduced through the bottom distributor, flows upward through the cation resin and out of the interface collector to waste. The caustic is added through the upper regenerant distributor which is located just above the resin bed, and flows downward through the anion resin and out of the interface collector to drain. Depending on the design, acid and the caustic may be added as separate regeneration steps or both may be added simultaneously.

After the acid and caustic treatments, the unit is given a short rinse, drained, and thoroughly mixed by air injected into the bottom distributor. The unit is then refilled with water and rinsed to waste until the effluent is of acceptable quality for return to service.

Mixed bed demineralizers can also be designed for regeneration external to the demineralizer service shell. In these units, the resins are sluiced to the regeneration facilities, separated by backwashing and regenerated in the normal manner. This method provides nearly continuous service from one unit in that a spare charge of freshly regenerated resin can be continuously available to replace exhausted resin removed from the unit. The method also reduces the chances of inadvertently contaminating the treated water with acid or caustic regenerants.

PART 5-OTHER PROCESSES

Recent developments in ion exchange have led to the use of new techniques for handling problems and to more economical demineralization approaches. One relatively new development has been the commercial application of continuous, counter-current ion exchange which uses ion exchange resins more efficiently than the traditional fixed-bed sys-

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tems. This process passes the water through the resin column so that it first penetrates nearly exhausted resin and progressively reaches resin in higher stages of regeneration until, just before leaving the column, it passes through freshly regenerated resin. Exhausted resin is frequently removed from the service cycle and regenerated in a separate part of the unit and then returned to the main vessel.

Another significant development uses layered resin beds, usually weakly basic and strongly basic anion resins, in the same column. Because the weakly basic resin is less dense than the strongly basic resin, backwashing after regeneration causes the weak base resin to form a layer on top of the strong base resin.

If the weak base resin is selected properly, the layer it forms will protect the strong base resin from organic fouling and will also economically remove mineral acidity. This can also be applied to cation units where weakly acidic (carboxylic) cation resin is used in the same vessel as strongly acidic cation resin. In both cases significant regenerant savings can result.

Applications and Advantages. Demineralization has produced high purity water for nearly every use. Demineralized water is widely used for high-pressure boiler feedwater, chemical process water, electronics production, pharmaceutical manufacture and academic research.

Demineralization systems can produce water of a purity comparable to that obtained by distillation, and with most fresh water supplies, at a fraction of the cost. Mixed bed demineralizers have produced water with a 77F specific conductance of 0.055 micromho. Demineralization systems are available in a wide range of sizes, from small laboratory columns, rated at only a few gallons per hour, to large units which can produce thousands of gallons per minute. Efficient operation can be obtained in nearly any size.

Limitations. Like other ion exchange systems, demineralizers will function efficiently only if the water supply is free from suspended matter and oxidizing materials such as chlorine. Anion exchange resins are more susceptible to organics. Standard demineralizer resins cannot remove colloidal or some organically sequestered materials and their unexpected presence has caused silica or iron contamination in some demineralized water supplies. While some organic materials will pass through demineralizer columns unaffected, others may seriously foul the anion resin beds.

PART 6-CONDENSATE POLISHING

A comparatively recent but very important application of ion exchange is condensate polishing. Industry has long recognized the inherent value of condensate and recovering it for return to the feedwater. However, as makeup water quality improved and as boiler operating pressures increased, the low level contaminants usually found in condensates began constituting the main problem for potential deposition and boiler tube failure.

Typically, the contaminants in condensate are iron, copper and low levels (ppb) of electrolytes resulting from carryover/entrainment. Those systems using brackish or even sea water for condensate cooling may experience condenser leakage, resulting in a high level of electrolyte contamination.

Industrially, process or steam condensates are available for return to the cycle at temperatures above 200F. This dictates the use of strong cation resin operating in the sodium cycle for polishing these condensates. The resin is stable at temperatures up to 270F. Also, the small amount of sodium added to the condensate by such treatment can normally be tolerated in most industrial systems.

Sodium zeolite softeners used in this service may be operated at flow rates in the range of 35 to 50 gpm per square foot, unlike conventional makeup water units which operate in the normal range of 6 to 8 gpm per square foot. This is because the ionic loading imposed by the condensate contaminants is very low. Also, the major contaminants are particulate iron and copper corrosion products. The exchanger filters these materials and this imposes no ionic loading.

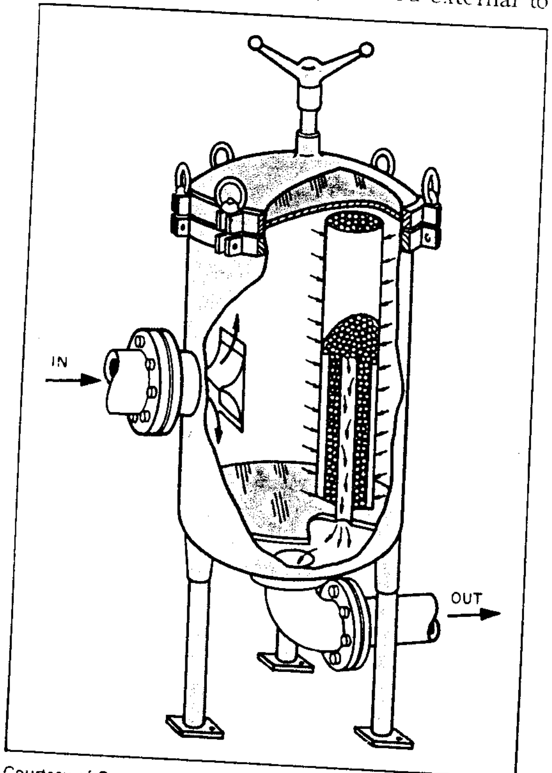
Regeneration of the sodium cycle condensate polishers is essentially the same as that for makeup softeners. Salt at a level of 15 pounds per cubic foot is used. However, a cleaning agent is also used with the brine to reduce iron which may have been oxidized from the ferrous to the ferric state. The iron may then be regenerated from the resin.

Resin selection for sodium cycle polishing service is another important consideration. Because of the high design flow rates, pressure drops approach 100 psi, and considerable force is exerted on the resin. The resin must have physical properties which permit it to withstand this force.

Also, because of the high pressure drop, the design of the exchange vessel must be such that the underdrain system will not collapse nor will it pass resin into the treated water stream. Two principal types are used: screen-wrapped header laterals and welded plates with small offset orifices. While these designs are very efficient, added protection is usually included in the form of a resin trap downstream of the units.

Systems requiring essentially complete ion removal, in addition to crud removal, use a mixed bed resin column. The temperature of the condensate so treated must be below 140F which is the maximum temperature for continuous operation of the strong anion resin used.

Mixed resin systems may be of two types. The first is the powdered resin, septum-coated system in which the resin is discarded after exhaustion. The second is the standard mixed bed (except for tank design mentioned above) in which the resin is regenerated. Frequently, mixed bed resins are regenerated external to the operating units to avoid possible regenerant contamination of the condensate.



Courtesy of Graver Water Div., Ecodyne Corporation

Figure 8-15. Powdered resin condensate polisher.

PART 7-TROUBLESHOOTING

As with any dynamic system involving mechanical equipment and chemical reactions, problems do occur in the operation of ion exchange systems. The problems are usually signalled by poor or off-spec water quality or a reduction in the total gallons of water treated during an exhaustion cycle.

Such difficulties may be classed in several broad groups of causes for problems which may be encountered. Investigating them in the order listed in the following will provide a guide in order of increasing complexity or extent of mechanical or laboratory involvement.

CHANGED OR VARYING WATER QUALITY

Well waters provide a comparatively constant quality. Surface waters, on the other hand, vary. Hardness varies as do other compounds. A hardness increase of 10 percent will result in a 10 percent reduction in the quantity of water softened during sodium cycle operation.

Subtle changes may also occur. For example, in a demineralization system which includes a decarbonator, efficiency may vary or degrade as a result of improper air/water flow or distribution. Carbon dioxide removal efficiency deteriorates and the resulting ionic load increase on the strong base anion unit results in less throughput per exhaustion cycle.

Regular chemical analyses of the influent to ion exchangers should be performed to reveal such variations.

IMPROPER REGENERATION SCHEDULE

Both service and regeneration flow rates influence quantity and quality of water treated by ion exchange. Manufacturers' recommendations should be followed.

REGENERANT QUALITY

Specifications for regenerant chemicals' quality are given by either the resin supplier or the equipment manufacturer. The regenerant quality specified should be used. Inferior grades will lead to problems.

For example, use of a caustic soda with high levels of iron or perchlorates will result in iron-fouled or chemically degraded anion resin.

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MECHANICAL

Included in this grouping of causes for ion exchange problems are:

1. High suspended solids loading which causes channeling and premature breakthrough.
2. Leaking valves which cause poor quality water in the treated water.
3. Broken or clogged distributors which result in poor water or regenerant distribution, causing off quality and/or short runs.
4. Resin loss because of excessive backwash flow or broken underdrain systems.
5. Clogged or plugged underdrains which cause excessive pressure drops, resulting in premature breakthrough as well as physical resin breakdown.

All the above mechanical deficiencies may be detected by a thorough equipment inspection. Corrective measures will be obvious. Monitoring devices should also be checked and calibrated regularly to insure that they are functioning correctly.

FOULED RESIN

Resin may become fouled with several contaminants which could be present in the supply being treated.

1. Iron may exist in water as a ferrous or ferric inorganic salt or as a sequestered organic complex. Ferrous iron will exchange, but ferric iron will not. As long as the iron remains in the ferrous state, it is regenerable even by salt from the cation resin. Ferric iron, on the other hand, will coat the cation resin and block exchange sites. Removal by an acid or a strong reducing agent with salt is required. Organically bound iron will pass through the acid cation in a demineralizer train and foul the anion resin. Cleaning procedures such as warm salt-warm caustic, acid, or even sodium hypochlorite washing will restore part of the lost capacity; 100 percent recovery is usually not attained.
2. Manganese present in some well water causes capacity loss in much the same manner as iron.

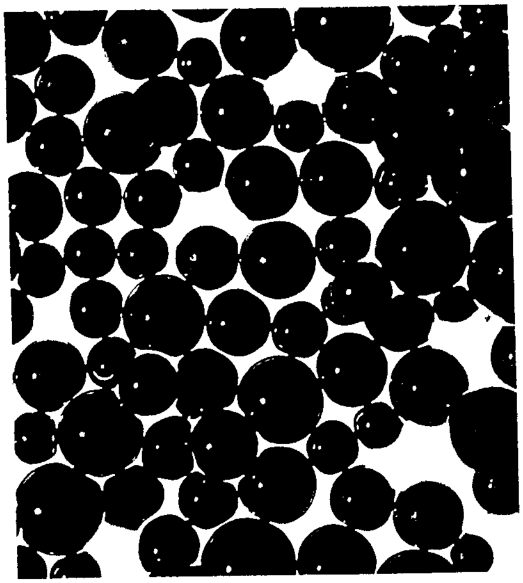

Figure 8-16. Iron-fouled resin.

3. Aluminum is rarely present in water in an ionic form that will permit exchange with cation resin. It is usually encountered as aluminum hydroxide resulting from alum or sodium aluminate used in clarification or precipitation softening. The aluminum floc, if carried through the filters, will coat the resin. If it occurs on cation resin operating in the sodium cycle, it may be removed by either acid or caustic cleaning because it is amphoteric. Aluminum is usually not a problem in demineralizers because removal occurs during acid/caustic regeneration.
4. Hardness precipitates may carry through filters associated with cold or hot precipitation processes. Even if carrythrough does not occur, precipitation can occur in ion exchangers following cold lime softeners because at ambient temperatures the precipitation reactions are not complete and may occur in downstream equipment. Also, precipitation potential exists when two or more precipitation softener effluents are blended. This is because the alkalinity and hardness are usually not the same in parallel units. When such waters are blended, the combined stream will approach equilibrium by precipitating hardness. An acidic cleaning

chemical will dissolve hardness precipitated on the resin.

5. Calcium sulfate precipitation may occur in cation exchangers operating on the hydrogen cycle. At exhaustion, the resin may be holding as much as two pounds of calcium per cubic foot. Sulfuric acid is the usual regenerant and if introduced at too high a concentration or if the regenerant addition flow rate is too low, calcium sulfate will precipitate.

   Cation resin severely fouled with calcium sulfate is usually discarded. In mild cases, hydrochloric acid may be used to promote the following reassociation of calcium and sulfate:

$$\underset{\text{calcium sulfate}}{CaSO_4} + \underset{\text{hydrochloric acid}}{2HCl} = \underset{\text{sulfuric acid}}{H_2SO_4} + \underset{\text{calcium chloride}}{CaCl_2}$$

   Because of the extreme insolubility of calcium sulfate, the cleaning will take considerable time and is usually performed external to the service vessel.

6. Oil fouling will cause no chemical degradation of a resin. However, the coating of resin with oil will produce agglomeration of the beads into large masses, thereby causing an increased pressure drop across the bed, channeling and premature breakthrough. Some surfactants are quite effective in removing oil fouling through regular maintenance or out-of-service cleaning procedures.

7. Microbiological fouling may be encountered since the growth may be supported by ion exchange resin beds. Organic compounds, ammonia, nitrates, etc. contained in the water serve as nutrients. Although such growth will not chemically degrade cation resins, it can result in problems such as increased pressure drop across the bed, plugged distribution laterals and highly contaminated treated water. Severe conditions may require the application of suitable sterilization agents.

   If the growth occurs in a cation unit preceding a strong base anion exchanger, waste organics generated by the microbes and organics resulting from decay of the microbes may foul the anion resin.

8. Polymerization of silica may occur in anion resin beds. At the start of a regeneration, silica is eluted in quantity. At exhaustion, the water in the anion unit is acidic. If flow rates are not correct, polymerization may occur in strong base units, although this is very rare.

   However, in a two-bed weak and strong anion system, use of all the waste regenerant from the strong base unit for regenerating the weak will likely cause polymerization in the weak base unit. This is avoided by wasting the first 20 to 25 percent of the regenerant from the strong base unit. Alternately, the weak base resin may be neutralized and partially regenerated by applying about one-half the weak base regenerant requirement as fresh caustic.

   Fortunately, a warm (120F) regeneration with fresh caustic will remove polymerized silica.

IRREVERSIBLE RESIN DETERIORATION

Oxidants. Oxidants, of which the most frequently encountered is chlorine, will degrade resin. Usually attack occurs on the cation resin. Anion units following cation units are not

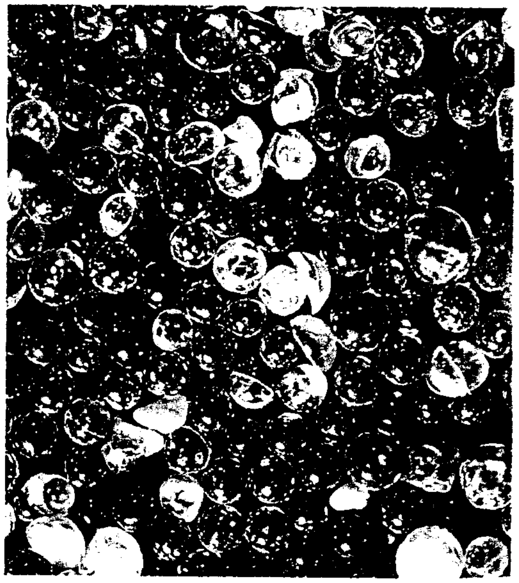

Figure 8-17. Calcium sulfate-fouled resin.

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affected because the oxidant is consumed in the cation exchanger.

Oxidants attack the divinyl benzene portion of cation resin, causing the resin to become mushy. While exchange sites are not affected, the mushy resin gives rise to increased pressure drop and often, severe channelling. The unit's "effective" capacity is thereby significantly reduced.

Oxygen in the treated water will not cause resin degradation except in sodium zeolite softeners following hot process softeners. To reduce this problem, resins with higher divinyl benzene content (12 percent) are used.

However, oxygen-saturated water, as in water following decarbonation, will attack certain weak base resins of the condensation type. This is in contrast to the divinylbenzene structure which is not affected.

It should be noted that degradation products of cation resin attack will organically foul strong base resins. Dechlorination with sodium sulfite should be standard practice for ion exchange treatment of chlorine-bearing waters. Dechlorination with sodium sulfite proceeds according to the following reaction:

$$\underset{\text{sodium sulfite}}{Na_2SO_3} + \underset{\text{chlorine}}{Cl_2} + \underset{\text{water}}{H_2O} = \underset{\text{sodium sulfate}}{Na_2SO_4} + \underset{\text{hydrochloric acid}}{2HCl}$$

One ppm of chlorine requires 1.78 ppm of sodium sulfite.

Organic Fouling. Perhaps the most serious problem which has confronted ion exchange application since its inception is the irreversible fouling of strong base anion resin. Usually, only insignificant levels of organics are found in well waters. However, surface waters may contain as much as hundreds of parts per million of natural and man-made synthetic organic matter. Natural organics are derived from decaying vegetation and are aromatic and acidic in nature, frequently complexed with a heavy metal such as iron. Terms such as tannins, tannic acid, humic and fulvic acid are used to describe these contaminants.

The effect of organics on anion resin is the degradation of the strong base sites (reduction of salt splitting capacity). The functionality will change from strong base to weak base and finally to neutral sites. Thus, a fouled resin may exhibit a good total capacity (reflecting the higher capacity of the weak base sites) and a very poor salt splitting capacity. Loss of salt splitting capacity will be reflected in reduced ability to remove carbonic and silicic acids.

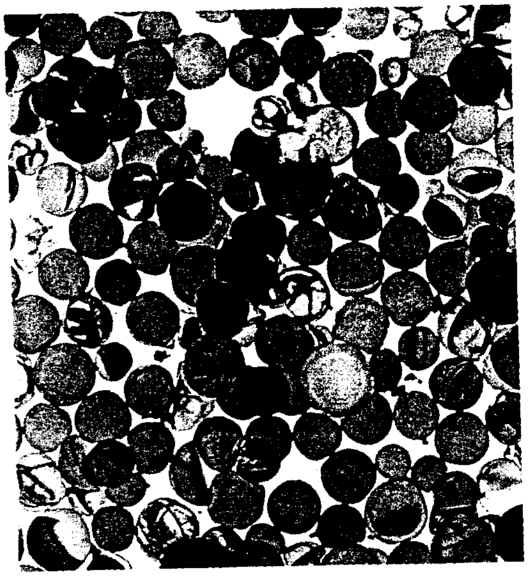

Figure 8-18. Organic-fouled resin.

Organic fouling of anion resin is reflected by a tea to dark brown colored wastewater during caustic addition and rinse. Operationally, the anion exchanger will show higher conductivity and lower pH water than uncontaminated resin produces.

The following methods are being used, alone or in combination, to reduce organics in the feed to a demineralizer:

1. Pre- and post-chlorination to oxidize organics with clarification and filtration.
2. Activated carbon filtration.
3. Macroporous resins (weak base) ahead of the strong anion to sorb organics.
4. Newer acrylic resins which have a high resistance to organic fouling and good strong base capacity.

Organic foulant removal from anion resin may be attempted by one or more of the following:

1. Alternate warm salt and caustic (120F).
2. Hydrochloric acid alone or in place of salt.
3. Solutions of 0.25 to 0.5 percent sodium hypochlorite.

Much of the organic contaminants will be eluted, but recovery of salt splitting capacity is usually not significant.

10

preboiler and boiler corrosion control

A major goal of any feedwater conditioning program is to protect the boiler and accessory equipment against corrosion during operation and when the system is out of service. Corrosion can occur in the preboiler system, comprising the external treatment system, deaerating equipment, feedwater lines, pumps, stage heaters and economizers. The most common causes of corrosion in boiler systems are dissolved corrosive gases, chemical agents, concentration cells and low pH. Corrosion problems can develop in any part of the steam generation system both on the water-side and fireside.

PREBOILER CORROSION AND CONTROL

Corrosive gases vary with the raw water source. When treatment chemicals are added to water for specific purposes, such as chlorine for control of organics (color), some residuals tend to be corrosive. Naturally occurring contaminants such as dissolved oxygen and carbon dioxide can normally be removed by proper deaeration equipment.

DISSOLVED OXYGEN AND REMOVAL

Oxygen is highly corrosive when dissolved in water. Even small concentrations of this gas can cause serious problems. Makeup water can introduce appreciable amounts of oxygen into the system. Other major sources of oxygen in the system are through leakage of air on the suction side of pumps, the breathing action of receiving tanks, and leakage of undeaerated water used for pump seals. Excessive leakage of such water into boiler feedwater can occur at such points, introducing oxygen as well as other undesirable contaminants, bypassing the normal deaeration equipment.

At 60F and atmospheric pressure, the solubility of oxygen in water is approximately 10 parts per million (ppm). The severity of oxygen attack depends on the concentration of dissolved oxygen, the pH and the temperature.

One of the most serious aspects of oxygen corrosion is that it occurs as pitting. A pit is a concentration of corrosion in a small area of the total metal surface. This type of corrosion can produce failures even though only a relatively small amount of metal has been lost and the overall corrosion rate is relatively low.

The influence of temperature on the corrosivity of dissolved oxygen is particularly important in closed heaters and economizers where water temperature increases rapidly. The temperature rise provides enough additional driving force to accelerate the reaction so that even very small quantities of dissolved oxygen in the feedwater can cause severe corrosion.

Mechanical deaeration of the feedwater is an important first step in eliminating dissolved oxygen and other corrosive gases such as ammonia, carbon dioxide and hydrogen sulfide.

Efficient mechanical deaeration will reduce dissolved oxygen to as low as 0.005 cc per liter (6.5 ppb). For complete oxygen removal mechanical deaeration requires chemical assistance. When mechanical deaeration is not available, chemical deaeration alone will be adequate for some, but not all, operating conditions. For most systems, economics favor both methods combined.

In boilers operating below 1,000 pounds per square inch (psi), the most commonly used agent for chemical deaeration is catalyzed sodium sulfite because of its low cost, ease of handling and non-scaling characteristics. The oxygen scavenging property of sodium sulfite is illustrated by the reaction:

$$\begin{array}{ccccc} 2Na_2SO_3 & + & O_2 & = & 2Na_2SO_4 \\ \text{sodium} & + & \text{oxygen} & = & \text{sodium} \\ \text{sulfite} & & & & \text{sulfate} \end{array}$$

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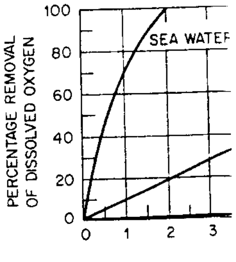

Figure 10-1. Reaction tir

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Theoretically 7.88 ppm of chemically pure sodium sulfite are required to remove 1.0 ppm of dissolved oxygen, but use of technical grades of catalyzed sodium sulfite, combined with the handling and blowdown losses of normal plant operation, usually requires feeding approximately 10 pounds of sodium sulfite for each pound of oxygen present in the feedwater. Also available are concentrated liquid solutions of catalyzed sodium sulfite whose feed requirements depend on their effective concentration. The concentration of excess sulfite maintained in the feedwater or boiler water will also influence this requirement.

Sodium sulfite must be fed continuously to achieve complete oxygen removal. Usually the most suitable point of application is the storage compartment of the deaerating heater. Where hot process softeners are followed by hot zeolite units, the recommended point of feed is to the filter effluent of the hot process unit (prior to the zeolite softeners) to protect the zeolite resin and shells. Feeding sodium sulfite intermittently is generally not recommended. But in certain low-pressure systems, where additions are made often enough to maintain proper residual concentrations, intermittent feeding has been satisfactory.

A number of factors affect the speed of the sulfite-oxygen reaction. The most important is temperature. As temperature increases, reaction time decreases so that, in general, every 18F increase in temperature doubles reaction speed. At temperatures of 212F and above, reaction is quite rapid. The presence of an excess or overfeed of sodium sulfite also increases reaction rate. The reaction proceeds most rapidly at pH values in the vicinity of 9.0 to 10.0.

Some natural waters inhibit the oxygen-sulfite reaction. Figure 10-1 shows reaction rates at room temperature between oxygen and sodium sulfite in three different types of waters. As may be seen, the reaction is fairly rapid with seawater, complete oxygen removal occurring in two minutes. In distilled water, only 75 percent of the oxygen is removed after 10 minutes of contact time. With a surface supply which has inhibitory properties, 10 minutes of contact time removes only about three percent of the oxygen.

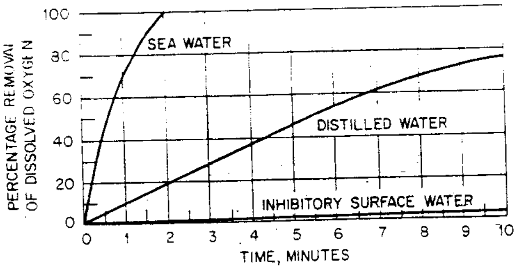

Figure 10-1. Reaction time, three different waters.

Research into increasing the speed of the oxygen-sulfite reaction indicates that certain materials will act as catalysts to speed up this reaction. The most effective catalysts are the heavy metal cations with valences of two or more. Iron, copper, cobalt, nickel and manganese are among the more effective materials. Combinations of several of these heavy metal cations have also been effective in speeding up the reaction at a continuing, dependable rate.

Research on catalytic aids for oxygen removal has produced a catalyzed sodium sulfite which combines suitable catalysts and sodium sulfite in one formulation. This assures a compound which will remove oxygen almost instantaneously in typical applications.

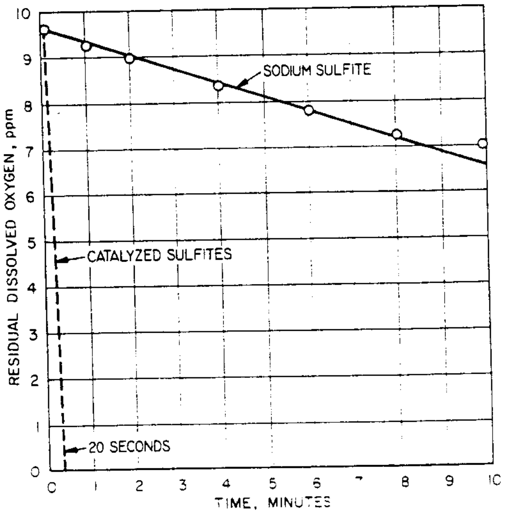

Figure 10-2. Sodium sulfite vs catalyzed sodium sulfite.

Figure 10-2 compares the removal of oxygen using commercial sodium sulfite and using catalyzed sodium sulfite, both at room temperature. As can be seen, after 10 minutes of contact, sodium sulfite has reduced the oxygen content from 9.8 ppm to just over 6.6 ppm, a very minor reduction. The catalyzed sodium sulfite, on the other hand, removes the oxygen completely in only 20 seconds, minimizing the corrosivity of the water due to dissolved oxygen.

19

condensate system corrosion

The problems resulting from iron and copper corrosion in condensate systems are not confined to the piping and equipment thus damaged nor to the attendant loss of high quality water and energy when condensate is lost. Corrosion products and process chemicals from corrosion-caused leaks, if returned to the boiler, can contribute to the formation of damaging boiler deposits, thereby reducing system reliability and increasing operating and maintenance costs.

CORROSION OF IRON IN WATER

Iron corrodes in water in the absence of oxygen because it is less noble than hydrogen. Iron replaces the hydrogen ion in water as shown below:

$$\begin{array}{ccccccccc} \mathrm{Fe} & + & \mathrm{2HOH} & = & \mathrm{Fe(OH)_2} & + & \mathrm{H_2} \\ \text{iron} & + & \text{water} & = & \text{ferrous hydroxide} & + & \text{hydrogen} \end{array}$$

In pure water the reaction product, ferrous hydroxide, elevates the pH by providing hydroxide ions as shown below:

$$\begin{array}{ccccc} \mathrm{Fe(OH)_2} & = & \mathrm{Fe^{++}} & + & \mathrm{2OH^-} \\ \text{ferrous hydroxide} & = & \text{ferrous ion} & + & \text{hydroxide ion} \end{array}$$

This reduces the amount of H^+ ions available to react. The reduction in hydrogen ions tends to retard the corrosion reaction. Secondly, the Fe^{++} reaction product, $Fe(OH)_2$, concentration is increased, reducing the electric potential or driving force for the reaction to proceed. If the temperature of the water rises, ferrous hydroxide is converted to magnetite in the absence of oxygen to form a somewhat protective film barrier, further retarding the reaction by physically separating the reactants as shown:

$$\begin{array}{ccccccc} \mathrm{3Fe(OH)_2} & = & \mathrm{Fe_3O_4} & + & \mathrm{2HOH} & + & \mathrm{H_2} \\ \text{ferrous hydroxide} & = & \text{magnetite} & + & \text{water} & + & \text{hydrogen} \end{array}$$

Above about 120F only magnetite is found. The preceding corrosion equations may be combined to give the overall reaction, in the absence of oxygen:

$$\begin{array}{ccccccc} \mathrm{3Fe} & + & \mathrm{4HOH} & = & \mathrm{Fe_3O_4} & + & \mathrm{4H_2} \\ \text{iron} & + & \text{water} & = & \text{magnetite} & + & \text{hydrogen} \end{array}$$

The above indicates that the corrosion of iron should be a self-limiting reaction proceeding to equilibrium and then slowing down to an almost immeasurable rate. This would hold true under carefully controlled laboratory conditions but not for an actual condensate system, since the condensate contains varying amounts of contaminants that promote the corrosion reaction, the most common being dissolved oxygen and carbon dioxide.

OXYGEN CORROSION

In the presence of oxygen, the corrosion mechanism of iron proceeds further. Ferrous hydroxide is unstable in the presence of oxygen, and ferric hydroxide will be formed. While ferrous hydroxide is a corrosion reaction retarding agent, ferric hydroxide is not. Thus the presence of free oxygen in a given system enhances the corrosion reaction. The iron-water-oxygen reaction resulting in the formation of ferric oxide may be summarized by the following equation:

$$\begin{array}{ccccccccc} \mathrm{4Fe} & + & \mathrm{6HOH} & + & \mathrm{3O_2} & = & \mathrm{4Fe(OH)_3} \\ \text{iron} & + & \text{water} & + & \text{oxygen} & = & \text{ferric hydroxide} \end{array}$$

Ferric hydroxide is virtually insoluble in water and precipitates out of solution. The precipitate formed by ferric hydroxide is not protec-

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tive. The effects of temperature and time produce ferric oxide as the final end product of the corrosion mechanism as illustrated below:

$$\underset{\text{ferric hydroxide}}{2Fe(OH)_3} + \text{temp/time} = \underset{\text{ferric oxide}}{Fe_2O_3} + \underset{\text{water}}{3HOH}$$

Oxygen corrosion is easily recognized by the large pits produced by this type of attack. Oxygen pitting begins at weak points in the iron oxide film and continues at the same location. The type of pit developed is influenced by the condensate pH. At low pH, the iron oxide layer is not particularly protective so pits tend to be larger. As the pH of the condensate increases, a protective oxide layer is more effectively maintained, resulting in pits of smaller circumference.

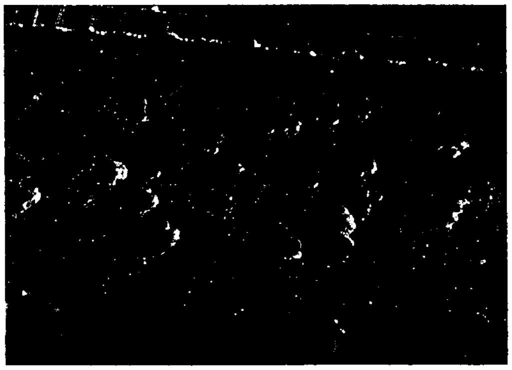

Figure 19-1. Typical oxygen pitting of condensate line.

Active oxygen pits contain reduced black oxide along the concave surface of the pit, while the surrounding area above the pit is covered with red ferric oxide. The presence of black iron oxide in oxygen pits indicates that the pit is active. If the pit contains red iron oxide, it indicates that the pit was active at one time but is no longer active. The black oxide layer is anodic with respect to the surrounding red oxide layers.

Oxygen can enter the condensate by direct absorption of air and by introduction with the feedwater and subsequent flashing over with the steam. Depending on the plant and operation, either source could predominate.

With proper mechanical deaeration and chemical oxygen scavenging, virtually all oxygen can be eliminated from boiler feedwater. Good system design is required to minimize air contact with the condensate and subsequent oxygen absorption. Condensate receiving tanks are common points in the system for air-condensate contact. This can be minimized by installing a cover on the receiver tank and a steam heating coil within the tank. The cover will reduce air contact while the steam coil will elevate condensate temperature, thus reducing oxygen solubility.

Under certain conditions gross oxygen contamination of the condensate may be unavoidable. In such cases (for example, condensate from warm up steam for intermittently used equipment), the condensate should be wasted to avoid severe attack of the lines between the point of condensation and the deaerating heater.

In most cases, proper feedwater deaeration and elimination of potential air infiltration into the condensate will substantially reduce oxygen corrosion in the condensate system.

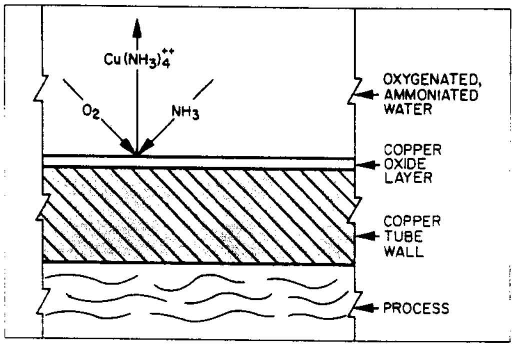

Figure 19-2. The protective copper oxide film can be destroyed by complexing agents such as ammonia.

OXYGEN CORROSION OF COPPER

The corrosion of copper by oxygen generally results in the formation of cupric oxide, and the reaction is in most cases self-limiting. If, however, copper complexing agents such as ammonia are present, the copper oxide film cannot become permanently established. As the oxidized copper that should form the copper oxide film is complexed and washed away, further oxidation of the base metal takes place. High concentrations of carbon dioxide in the condensate system, at lower pH values (less than 8) have an effect similar to ammonia in dissolving the copper oxide film. Both conditions, high ammonia concentrations and low pH with carbon dioxide, should be avoided in systems containing copper-bearing equipment.

CARBON DIOXIDE CORROSION

As carbon dioxide dissolves in water, it causes the pH to be depressed by increasing the hydrogen ion concentration as shown in the reaction sequence below:

$$\begin{array}{ccccc} CO_2 & + & HOH & = & H_2CO_3 \\ \text{carbon} & + & \text{water} & = & \text{carbonic} \\ \text{dioxide} & & & & \text{acid} \end{array}$$

$$\begin{array}{ccccc} H_2CO_3 & = & H^+ & + & HCO_3^- \\ \text{carbonic} & = & \text{hydrogen} & + & \text{bicarbonate} \\ \text{acid} & & \text{ion} & & \text{ion} \end{array}$$

$$\begin{array}{ccccc} HCO_3^- & = & H^+ & + & CO_3^= \\ \text{bicarbonate} & = & \text{hydrogen} & + & \text{carbonate} \\ \text{ion} & & \text{ion} & & \text{ion} \end{array}$$

Carbonic acid promotes the iron corrosion reaction by supplying a reactant, H^+. The overall reaction is:

$$\begin{array}{ccccccc} 2H_2CO_3 & + & Fe & = & Fe(HCO_3)_2 & + & H_2 \\ \text{carbonic} & + & \text{iron} & = & \text{ferrous} & + & \text{hydrogen} \\ \text{acid} & & & & \text{bicarbonate} & & \end{array}$$

Ferrous bicarbonate is soluble under many conditions and behaves like ferrous hydroxide, i.e., as a corrosion reaction retardant. Bicarbonates are weak bases and mildly elevate solution pH values; ferrous ions reduce the driving potential of the reaction.

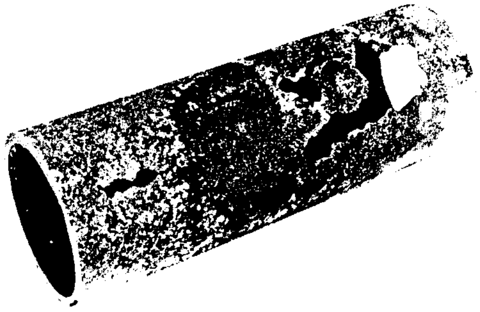

Figure 19-3. Section of condensate line destroyed by carbon dioxide (low pH) corrosion. Metal destruction is spread over a relatively wide area, resulting in thinning.

Ferrous bicarbonate stability in solutions is affected by heat, pH and the partial pressure of carbon dioxide above the condensate. Often one of these conditions changes from one location to another in the condensate system. Consequently, it is not unusual to find accumulations of corrosion products some distance from the actual corrosion site. The actual deposit formed can be one of a number of different hydroxides, oxides or carbonates of ferric or ferrous iron.

Carbon dioxide enters the system either as the dissolved gas or combined in the bicarbonate or carbonate alkalinity of the feedwater. Dissolved carbon dioxide will be removed from the feedwater by a properly operated deaerating heater, but the combined carbon dioxide will remain in the feedwater.

In the boiler the carbon dioxide is liberated as shown in the following:

$$\begin{array}{ccccccc} NaHCO_3 & + & \text{heat} & = & NaOH & + & CO_2 \\ \text{sodium} & + & \text{heat} & = & \text{sodium} & + & \text{carbon} \\ \text{bicarbonate} & & & & \text{hydroxide} & & \text{dioxide} \end{array}$$

$$\begin{array}{cccccc} Na_2CO_3 & + & H_2O & + & \text{heat} & = \\ \text{sodium} & + & \text{water} & + & \text{heat} & = \\ \text{carbonate} & & & & & \end{array}$$

$$\begin{array}{ccc} 2NaOH & + & CO_2 \\ \text{sodium} & + & \text{carbon} \\ \text{hydroxide} & & \text{dioxide} \end{array}$$

The first reaction proceeds to completion while the second is only approximately 80 percent completed. The net results are release of 0.79 ppm of carbon dioxide for each ppm of sodium bicarbonate as $CaCO_3$ and 0.35 ppm for each ppm of sodium carbonate as $CaCO_3$.

Carbon dioxide corrosion of condensate piping is more of a generalized loss of metal than the localized pitting which typifies oxygen corrosion. Thinning of the pipe wall occurs particularly in the lower portion of the pipe circumference. Grooving at the bottom of the pipe often results with failures occurring first at threaded sections.

The potential for carbon dioxide corrosion in a condensate system can be reduced by lowering the alkalinity of the makeup water by various external treatment methods.

SOURCES OF AMMONIA

Ammonia is usually present in condensate in low concentrations. The most common sources of ammonia in condensate are breakdown of nitrogenous organic contaminants and partial decomposition of hydrazine or amine-type treatment chemicals. In some cases, primarily in very high pressure systems, ammonia is fed to the system to control condensate pH. Good control must be exercised since it is aggressive toward copper-bearing alloys.

Ammonia, like carbon dioxide, is chemically bound in boiler feedwater. Unlike carbon dioxide, the higher the pH of the feedwa-

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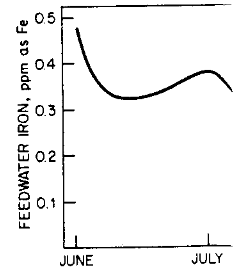

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CHEMICAL TREATMENT OF CONDENSATE SYSTEMS

Condensate systems can be chemically treated to reduce metal loss caused by oxygen and carbon dioxide corrosion. The treatment chemicals consist of neutralizing amines, filming amines, hydrazine, and in some cases ammonia.

Neutralizing Amines: Neutralizing amines neutralize the acid (H^+) generated by the solution of carbon dioxide in condensate. They hydrolyze in water to generate hydroxide ions required for neutralization:

$$\underset{\text{neutralizing amine}}{R\text{-}NH_2} + \underset{\text{water}}{H_2O} = \underset{\text{ammonium ion}}{R\text{-}NH_3^+} + \underset{\text{hydroxide ion}}{OH^-}$$

The overall neutralization reaction can be written as shown below:

$$\underset{\text{neutralizing amine}}{R\text{-}NH_2} + \underset{\text{carbonic acid}}{H_2CO_3} = \underset{\text{ammonium ion}}{R\text{-}NH_3^+} + \underset{\text{bicarbonate ion}}{HCO_3^-}$$

By regulating the neutralizing amine feedrate, the condensate pH can be elevated to within a desired range (e.g., 8.5 to 9.0).

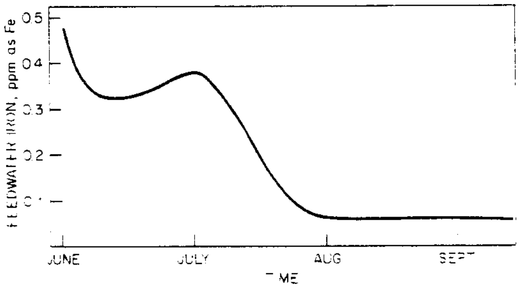

Figure 19-4. Feedwater iron determination is one method of monitoring the effectiveness of an amine treatment program.

There are numerous amines that can be used for condensate pH neutralization and elevation. The selection of the appropriate amine is controlled by the basicity, stability and distribution ratio characteristics of the particular amine.

The distribution ratio (DR) of an amine is expressed as:

$$DR = \frac{\text{amine in vapor phase}}{\text{amine in water phase (condensate)}}$$

Amines with a distribution ratio greater than 1.0 have more amine in the vapor phase than in the water phase. Conversely, amines with a distribution ratio less than 1.0 have more amine in the water phase than in the vapor phase.

The distribution ratios at atmospheric pressure of commonly used neutralizing amines are:

morpholine	0.4
diethylaminoethanol	1.7
dimethylisopropanolamine	1.7
cyclohexylamine	4.0
ammonia	10.0

The distribution ratio is a function of the pressure and temperature in the boiler and condensate system. Figure 19-5 shows how the distribution ratios of diethylaminoethanol and cyclohexylamine vary with pressure.

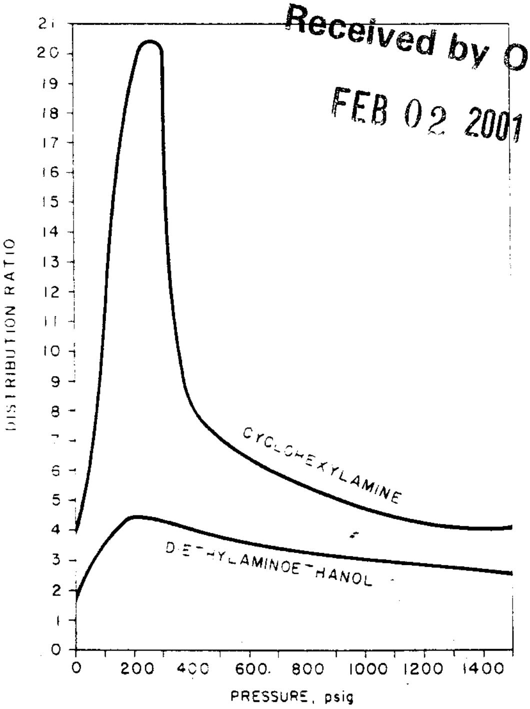

Figure 19-5. Graph snows how the distribution ratios of cyclohexylamine and diethylaminoethanol vary with pressure.

Ammonia has a low basicity, low molecular weight, and high distribution ratio. Thus, a significant amount of ammonia can be lost through the deaerator vent. Cyclohexylamine is more strongly basic and more chemically bound to the feedwater in the deaerator. In the deaerator, cyclohexylamine has a lower volatility, which further cuts down losses. Cyclohexylamine, as well as other neutralizing amines, does not complex copper as does ammonia.

In boiler systems where the bulk of the steam produced is used for turbine supply, morpholine is most suitable or a high morpholine blend material can be used. Morpholine, with a low distribution ratio, will be present in the initial condensate formed at the wet end of the turbine. In plants with extensive runs of steam lines, a material with a high distribution ratio is more desirable. In practice, best protection is provided by blended amine products containing a variety of materials with differing distribution ratios.

The quantity of neutralizing amine required depends on the carbon dioxide content of the condensate and the degree of corrosion protection desired. Complete neutralization will be achieved when the condensate pH in all portions of the system is above 8.3. From a practical standpoint, it is necessary to select one sampling point and establish a pH control range for that point that will correlate to the desired degree of protection for the system and/or to the desired level of iron in the condensate and feedwater.

The degree of protection afforded against piping and equipment failure in the condensate system and against iron deposition in boilers can be monitored by various means including corrosion test specimens installed in bypass racks, iron analyses, corrosion rate meters and submicron corrosion product filtration.

The behavior of amine bicarbonate in the deaerator will affect amine requirements for the system. Amine bicarbonates, though soluble in most cases, remain associated in the condensate. In an ideal situation, the amine bicarbonate entering the deaerator will break down with the subsequent venting of carbon dioxide to the atmosphere, and the recirculation of the amine back to the boiler. Actual behavior includes some loss of amine additive and some recirculation of carbon dioxide. The amounts of lost amine and retained carbon dioxide are a function of the amine bicarbonate stability in the deaerator.

Filming Amines. Another approach to preventing return line corrosion is the use of film-forming chemicals to lay down a protective film on metal surfaces. This approach has come into widespread use with the development of suitable products containing long-chained nitrogenous materials. Filming amines provide protection from both carbon dioxide and oxygen.

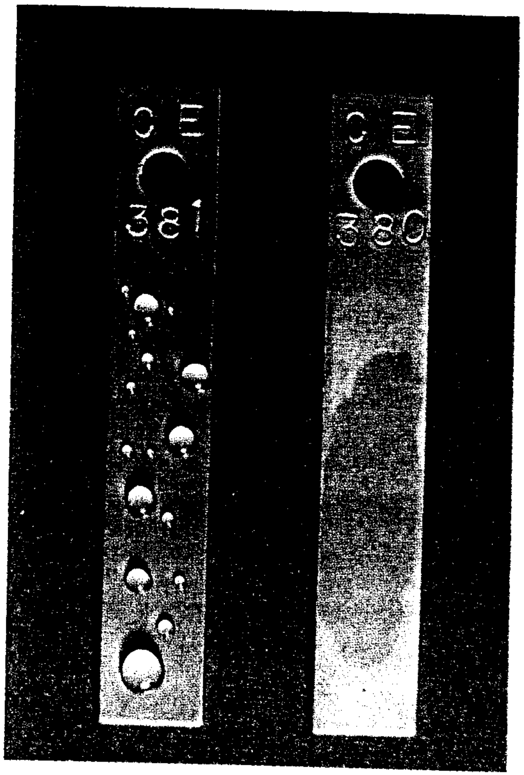

Figure 19-6. Test specimen 381 has a good octadecylamine film as shown by the non-wettable surface. Specimen 380 is untreated.

Filming amines function by forming a protective barrier against oxygen and carbon dioxide corrosion by replacing the loose oxide scale on the metal surfaces of the system with a very thin amine film. During the period of initial film formation, corrosion products are lifted off the metal surface by the surfactant properties of the filming amine. The metal is cleansed of oxides which would normally cling very tightly and possibly remain for a considerable period of time. For this reason, treatment in an older condensate system must be applied slowly and carefully. Excessive treat-

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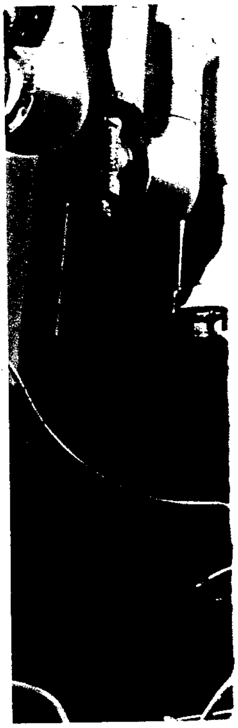

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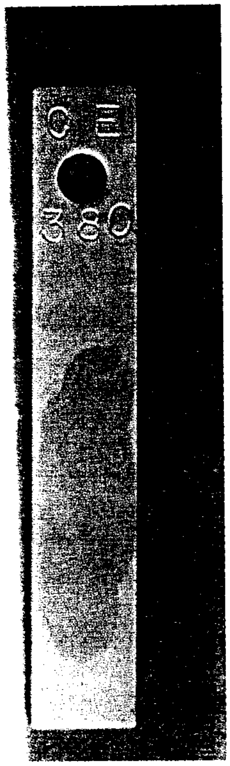

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Figure 19-7. Test specimen bypass rack used to monitor amine treatment. Corrosion rate meter on right measures instant corrosiveness values.

ment in the initial stages would cause large amounts of iron oxide to be sloughed off and be brought back to the boiler too quickly.

When contamination is present in the condensate, filming amines have a tendency to form deposits since they react with multivalent ions such as sulfate, hardness and iron ions. Overfeed of filming amines and excessive oxygen contamination can also contribute to this type of problem.

For maximum efficiency and to avoid the possibility of deposits in the boiler resulting from the tendency for the amine to react with boiler water multivalent ions, filming amines should be fed directly to the steam header.

Advances have been made in formulating filming amine treatments, particularly by blending with emulsifiers and dispersants. Straight filming amines, containing one ingredient such as octadecylamine, are effective, but can give problems in coverage and condensate line fouling. By blending in emulsifiers, and in some cases small portions of neutralizing amines, the film is spread out, giving more uniform coverage, increasing the protection from the filming amine, and significantly reducing the fouling potential. Application experience has shown that combination amines (filming amines with neutralizing amine dispersant aids) provide a superior film bond, reduce deposit problems and give better coverage and thus provide complete and more economical corrosion protection.

Filming amines are generally fed based on the steam throughput. Different levels of filming amines are required, depending on the particular blend in use. As in the case of neutralizing amines, various methods are used to monitor the effectiveness of the treatment including corrosion test specimens installed in bypass coupon racks, iron analyses, corrosion rate meters and submicron corrosion product filtration.

Hydrazine. Where oxygen intrudes into the condensate system, corrosion of iron and copper-bearing components can be controlled by injection of hydrazine. Since hydrazine decomposes in most boilers and superheaters and has a low distribution ratio, hydrazine present in the feedwater generally does not carry through to the condensate. Therefore, it is necessary to feed hydrazine close to the problem area. An example of this is the injection of hydrazine to the last stages on the exhaust trunk of a turbine to protect the condenser.