

Technology for Chemical Cleaning of Industrial Equipment

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NACE International—The Corrosion Society

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PREFACE

During the past 30 years, there have been significant improvements in the technology utilized to chemically clean industrial equipment. New organic acid and chelant solvents have been developed. New inhibitors and improved techniques for removing refinery/chemical plant deposits have been discovered. Most importantly, there have been significant improvements to our understanding of the chemical mechanisms that underlie many of these processes. This book will review technological areas where there have been new developments that have affected the commercial use of chemicals to clean industrial equipment. The content will emphasize the mechanistic understanding that underlies the important cleaning processes and solvents.

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1

INTRODUCTION

Industrial chemical cleaning involves the use of reactive chemicals to remove unwanted deposits from the surfaces of various pieces of process equipment. Included are components of power-generating units such as boilers and condensers, heat exchangers in refineries and petrochemical plants, and other industrial equipment such as digesters in paper mills. The chemical removal of unwanted surface deposits is conducted for many reasons. The first reason is to eliminate scales that contribute to increased corrosion. Examples of these types of deposits include iron oxides and copper found on the watersides of many types of process equipment. The second reason is to increase heat transfer. While steel may have a thermal conductivity of $300 \frac{\text{BTU} \cdot \text{in}^*}{\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F}}$, a highly conductive deposit such as magnetite (Fe_3O_4) has a thermal conductivity of only $20 \frac{\text{BTU} \cdot \text{in}}{\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F}}$. Very refractory deposits (various silicates) have conductivity values of $0.7 \frac{\text{BTU} \cdot \text{in}}{\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F}}$ (similar to fire brick). The third reason is to increase fluid flow rates and decrease pressure drops. The pressure drop of a fluid in a pipe at a constant flow rate is inversely proportional to the cube of the pipe diameter. Thus, small changes in pipe diameter may have large effects on flow rate and pressure drops. Utility power-plant surface condensers are regularly cleaned to increase the vacuum caused by condensing the steam. A clean condenser may have a vacuum that increases the boiler output by as much as 50 MW compared to a fouled unit. Fourth, spalling deposits may be removed to reduce damage to downstream components. Superheat and reheat sections of power-generating plants are cleaned to reduce damage to turbines from sloughed magnetite. The fifth reason is to “safe” vessels by removing toxic (i.e., benzene) or flammable (hydrocarbon) vapors prior to vessel entry. Refinery towers and tanks are frequently cleaned for these reasons.

Industrial chemical cleaning developed as an offshoot of the technology devised to increase the flow from oil, gas, and brine from wells. Hydrochloric acid was used prior to 1930 to dissolve deposits from oil wells. The development of the first corrosion inhibitors by John Grebe¹ in 1935 allowed acid to be used (in about 1939; see review of cleaning history by Nesbitt²) to remove deposits from industrial boilers. The

* $1 \frac{\text{BTU} \cdot \text{in}}{\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F}} = \frac{\text{Cal}}{2900 \text{ sec} \cdot \text{cm} \cdot ^\circ\text{C}}$

first utility power boilers were cleaned in about 1941 by using inhibited hydrochloric acid. Since that time, technology has been created to remove iron oxides and copper from boilers, to dissolve carbonate and silica deposits from a variety of systems, and to remove many types of refinery/petrochemical foulants. Methods have been invented to clean nuclear steam generators and components in paper mills and to chemically and mechanically treat the resulting wastes. There have been important advances made to the science of corrosion inhibition as applied to cleaning solvents, and to the use of low-toxicity chelating agents and organic acids. Several books have been written that cover aspects of the chemical cleaning technologies. McCoy reviewed the technology up to 1981.³ Wackenhuth⁴ produced a “How To” manual covering the chemical cleaning of fossil-fueled steam-generating equipment. NACE International⁵ published a Manual of Chemical Cleaning. Moniz⁶ reviewed methods used to clean chemical process equipment. The Chemical and Mechanical Cleaning Unit committee (T-3M) of NACE International’s Technical Practice Committee⁷ produced three volumes of bibliographic information on cleaning technology. Gutzeit⁸ reviewed methods for cleaning refinery and process equipment that stressed the use of good planning and control procedures.

TABLE 1
Summary of Common Inorganic Scale Forming Compounds¹⁰

Mineral Name	Common Name	Chemical Formula
	Hydrous ferric oxide	FeOOH
	Iron chromium spinels	CrFe ₂ O ₄
Acnrite	Sodium iron silicate	NaFe(SiO ₃) ₂
Analcite	Sodium aluminum sulfate	NaAlSi ₂ O ₆ · H ₂ O
Anhydrite	Calcium sulfate	CaSO ₄
Aragonite	Calcium carbonate-rhombic	CaCO ₃
Barite	Barium sulfate	BaSO ₄
Bricite	Magnesium hydroxide	Mg(OH) ₂
Chalcocite	Copper sulfide	Cu ₂ S
Chalcopyrite		CuFeS ₂
Copper		Cu
Covellite	Copper sulfide	CuS
Cuprite	Copper oxide	Cu ₂ O
Hematite	Ferric oxide	Fe ₂ O ₃
Hydromagnesite	Magnesium carbonate and hydroxide	3MgCO ₃ · Mg(OH) ₂ · 3H ₂ O
Hydroxyapatite	Calcium phosphate	Ca ₁₀ (OH) ₂ (PO ₄) ₆
Magnesia	Magnesium oxide	MgO
Magnetite	Ferric-ferrous oxide	Fe ₃ O ₄
Montmorillonite	Aluminum silicate	Al ₂ O ₃ · 4SiO ₂ · 4H ₂ O
Noselite	Sodium aluminum silicate	Na ₈ Si ₂ O ₇ O ₂₄ · H ₂ O
Pyrolusite	Manganese dioxide	MnO ₂
Serpentine	Magnesium silicate	Mg ₃ Si ₂ O ₇ · 2H ₂ O
Silica	Quartz	SiO ₂
Sodalite	Sodium aluminum silicate	Na ₈ Al ₆ Si ₆ O ₂₄ · Cl ₂
Troilite, pyrrhotite	Iron sulfide	FeS
Wusite	Ferrous oxide	FeO

This book is an expansion of a Corrosion/98 report⁹ and will review chemical cleaning technology developed since about 1965, with emphasis on understanding the chemical basis of the processes used to clean industrial equipment. Each section contains a review of a major technological area where there has been significant published information. The review process includes emphasizing the technology that actually reached or affected the market place as opposed to the technology that resides only in patents and academic documents. There will be some duplication, since areas covering corrosion/passivation/inhibitors also apply to technology to remove inorganic deposits such as iron oxide and copper. For clarity, some of the technology

TABLE 2
Cleaning Solvents in Current Use

Deposit	Solvents	Use Conditions
Iron oxide	5–15% HCl	150–180°F (65–82° C)
	Hydroxyacetic/formic acids	180–200°F, circulating (82–93° C)
	Monodiammonium citrate	180–275°F, circulating (82–135° C)
	Monosodium citrate	180–200°F, circulating (82–93° C)
	Ditetra-ammonium EDTA	200–300°F, circulating (93–149° C)
	or EDTA–organic acid mixtures	150–200°F, circulating (65–93° C)
	Sodium HEDTA, pH 1.4	100–150°F, circulating (38–65° C)
Copper Copper oxides	Triammonium EDTA/N ₂ H ₄	180–200°F, circulating (82–93° C)
	Thiourea derivative in HCl	150–170°F (65–77° C)
	Ammonium bromate	120–170°F (49–77° C)
	Ammonium persulfate	<100°F (38° C)
	Ammonium carbonate/O ₂ /NH ₃	<150°F (65° C)
	Ammonium EDTA (w Fe & oxidizer)	120–170°F (49–77° C)
	Ammonium citrate/oxidizer	120–170°F (49–77° C)
Calcium/magnesium carbonate	5–15% HCl	<150°F (65° C)
	Tetrasodium EDTA	180–300°F, circulating (82–149° C)
	7–10% sulfamic acid	<140°F (60° C)
Calcium sulfate	Tetrasodium EDTA	180–300°F, circulating (82–149° C)
	1% NaOH, then 5% HCl	100–150°F, circulating (38–65° C)
	EDTA–organic acid mixtures	120–150°F, circulating (49–65° C)
Calcium phosphate compounds	5–10% HCl	100–150°F (38–65° C)
	7–10% sulfamic acid	below 140°F (60° C)
	Tetrasodium EDTA	180–300°F, circulating (82–149° C)
Silica and silicate compounds	Alkaline boil with soda ash or NaOH	Alkaline boil at 50–100 psi (0.34–0.68 MPa)
	HCl with fluoride	150–170°F (65–77° C)
Sulfides	5–10% HCl	Heat slowly and scrub or flare H ₂ S
	5–10% HCl with aldehydes	100–160°F (38–71° C)
	5–15% H ₂ SO ₄ with aldehydes	100–160°F (38–71° C)
Disulfides	Chromic acid, followed by HCl	Hot chromic acid, 7–10% HCl, 5%
Organic despots	Detergents	150–250°F, circulating (65–121° C)
	Terpene emulsions	150–250°F, circulating
	Organic solvents (incl. chlorinated)	150–250°F, circulating
	Alkaline KMnO ₄ , followed by HCl and oxalic acid	

developed prior to 1965 will be noted so that there can be a comparison with more recent developments. The references, tables, and figures are contained within the following eight major sections: 1, Introduction; 2, Solvents for Removing Inorganic Deposits; 3, Mechanistic Studies of Iron and Copper Removal; 4, Corrosion, Passivation, and Inhibition; 5, Solvents for Removing Organic/Mixed Deposits; 6, Disposal of Chemical Cleaning Wastes; 7, Cleaning Nuclear Equipment; and 8, Special Techniques.

COMMON DEPOSITS AND SOLVENTS

The majority of fouling deposits that form in process equipment have their origins in the process fluids themselves. Water-based fluids can transport and deposit a wide variety of minerals. In addition, corrosion products form as a result of the reaction of the aqueous fluids with the metals of construction. Hydrocarbon and petrochemical fluids transport and deposit a variety of organic compounds, most of which will include polymeric materials. Hydrocarbons also can transport sulfides and mercaptans, which can react with the construction materials to form iron or copper sulfides. Table 1 shows a summary of common inorganic scale-forming compounds. Listed in Table 2 are some of the types of cleaning agents used in current practice to remove many of these types of fouling deposits.

The remaining sections of this book will review, in detail, many of the technologies embodied in the solvents and processes listed in Table 2.

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2

SOLVENTS FOR REMOVING INORGANIC DEPOSITS

The inorganic deposits described in Table 1 of Chapter 1 usually are formed on the surfaces of heat transfer equipment such as power and waste-heat boilers and heat exchangers, and in the various parts of cooling water systems. Iron oxides, copper, and calcium-containing deposits make up the largest portion of the material that requires removal from the metallic surfaces. We will review major developments for the chemical removal of each category of scale.

TECHNOLOGY FOR REMOVING IRON OXIDE DEPOSITS

There are a very large number of solvents for removing iron oxide deposits. They include mineral acids, organic acids, chelating agents, and mixtures of these chemical classes. The choice of a particular solvent system depends on the metal of construction, exact type and density of the oxide, and cost and disposal considerations.

Mineral Acids

Mineral acids used in chemical cleaning operations include hydrochloric acid (HCl), hydrofluoric acid (HF), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), nitric acid (HNO₃), and sulfamic acid (H₂NSO₃H). Most of these acids have very low pK_a values (see Table 1) and are completely ionized at the use strength. An exception is HF, which has a pK_a value similar to that of formic acid, and phosphoric acid, which is about 10 times as ionized as HF.

These acids were the first materials used to remove fouling deposits. The development of corrosion inhibitors¹ to protect metal in contact with the various mineral acids allowed the chemical cleaning industry to provide safe, useful services.

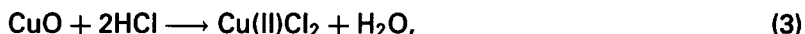
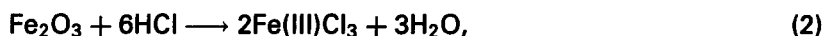
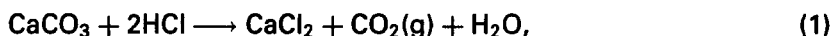
Hydrochloric acid is the simplest, most common, and most versatile mineral acid. This acid is used on virtually all types of industrial process equipment. It is used at strengths from 5% to 28% (5–10% is the most usual range), and it can be inhibited at temperatures up to about 180°F (82°C) (oilfield acids are used up to about 350°F

TABLE 1

Acid Disassociation (pK_a) Values for Mineral Acids

Acid	Mol. Weight	pK_1	pK_2	pK_3
Hydrochloric	36	-7		
Hydrofluoric	20	3.18		
Sulfuric	98	-3	2.0	
Phosphoric	98	2.1	7.2	11.9
Nitric	63	-1.6		
Sulfamic	97	1.0		

(177°C), but different standards of protection apply). Hydrochloric acid usually is not used to clean Series 300 stainless steel, free machining alloys, magnesium, zinc, aluminum, cadmium, or galvanized steel. Dangers to the metals of construction due to general or localized attack² limit the use of HCl for cleaning the previously mentioned metals. Most other metals of construction can be adequately protected during cleaning by using corrosion inhibitors (see Chapter 4). HCl will dissolve carbonates, phosphates, some sulfate scales, ferrous sulfide, iron oxides, and copper oxides. With the use of additives, fluoride deposits, copper, and silica also can be removed from surfaces with inhibited HCl. The equations listed below represent the basic reactions with HCl.



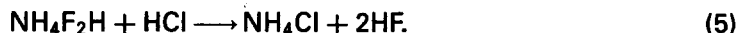
Sulfate and phosphate scales are converted to the more soluble chloride salts by the action of HCl.

Some recent documents concerned with the use of HCl in chemical cleaning are reviewed. Samuel³ described the use of HCl and other solvents for dissolving various deposits. The author concludes that HCl is effective for removing carbonate, phosphate, copper oxide, silicate, and iron oxide deposits. Trabanelli⁴ used a dynamic loop to compare cleaning effectiveness and corrosion produced by inhibited 7.5% HCl at 167°F (75°C) or inhibited 1.5% formic acid:1.5% hydroxyacetic acid mixtures (HYFor) used at 194°F (90°C). The HCl solvent was much more aggressive as a solvent than HYFor, especially for magnetite that was not electrically coupled to steel. Electrochemical tests performed during the acid cleaning indicated that initially the HCl solvent was highly corrosive. However, by the end of the cleaning test, the solvent was not substantially more corrosive than clean, inhibited acid. A likely cause of the initial corrosion is attributed to the release of ferric ions from the scale on the tubes being cleaned.

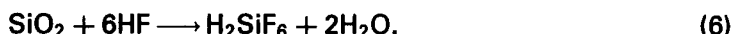
Ruiz⁵ reviewed a number of solvents for cleaning boilers. According to the author, the advantages of HCl include low cost, ability to dissolve a variety of deposits, and readily available corrosion inhibitors. Negative aspects of the use of HCl are its limited ability to dissolve copper (without thiourea); there are limitations on its use for cleaning Series 300 stainless steel, and HCl cleanings have high water usage because they require many rinses.

Rusch⁶ made a similar review of solvents for use in cleaning paper mill equipment. The same considerations apply for the use of HCl in paper mills as in boilers and other equipment.

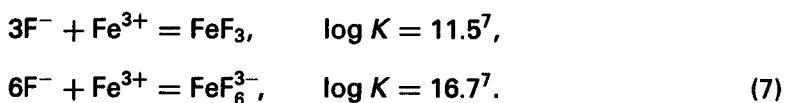
Additional mineral acids include HF, which is used with HCl to remove silica-containing deposits. In the U.S., HF usually is generated by adding ammonium bifluoride ($\text{NH}_4\text{F}_2\text{H}$ or $\text{NH}_4\text{F}\cdot\text{HF}$) to HCl:



The generated HF reacts with silica to form a more soluble fluorosilicic acid:



Problems can be encountered if the deposits contain calcium or magnesium salts that could precipitate CaF_2 or MgF_2 . Another advantage of the use of HF or HF-containing solutions is the partial control of ferric iron corrosion (see Chapter 4). Fluoride ions form very stable complexes with ferric ions:



Bradley and Smith⁸ reported that corrosion rates of exposed steel were much lower when mixtures of HF and HCl were used to dissolve magnetite, as compared with the use of HCl alone. In both cases, an organic corrosion inhibitor was used to control the attack of the acid on the steel. Lower corrosion rates also were reported for HF solutions compared with similar concentrations of HCl. Similar results were noted by Alfandry et al.⁹ Poff also described the benefits of adding ammonium bifluoride (ABF) to acidic solvents. This compound decreased the corrosion rates of the acidic solvents.¹⁰ Fluorides also were reported to increase the rate of iron oxide dissolution in several solvents.¹¹ Discussions of possible mechanisms are included in Chapter 4. Bieller¹² described the advantages of the use of HF as a boiler solvent. These include lower corrosion rates and increased cleaning rates compared with the use of HCl solvents.

Inhibited solutions of phosphoric acid were used for many years to clean surfaces. Rusch¹³ patented a formulation containing phosphoric acid and a corrosion inhibitor. After the iron oxide was dissolved, sodium hydroxide and an oxidizer (sodium nitrite) were added to passivate the surfaces. Mixtures containing HCl, phosphoric acid, citric and oxalic acid, and an amine (such as hexamethylenetetramine) were claimed by Garcia^{14–18} to be noncorrosive solvents for cleaning surfaces. It also was claimed that the “buffered acid solvents” were not harmful to skin or other “low oxidation state materials.” The author proposes that the conjugate bases from the organic acids control the amount of hydronium ions (H_3O^+) available to attack the substrates. Lau and Stadig¹⁹ described similar technology. This study reports on the use of “highly buffered acids” for the cleaning and passivation of heat exchangers. It is claimed that additional inhibitors are not needed during the acid treatment, which lasted for 2–3 h at 140°F (60°C). The formation of insoluble iron oxalates and phosphates may cause some of the inhibition described. The exchangers were flushed with water and not given an additional passivation treatment.

Sulfuric acid diluted to 10–20% can be used to clean Series 300 stainless steel as well as other metals (excluding aluminum galvanized steel or magnesium). This acid

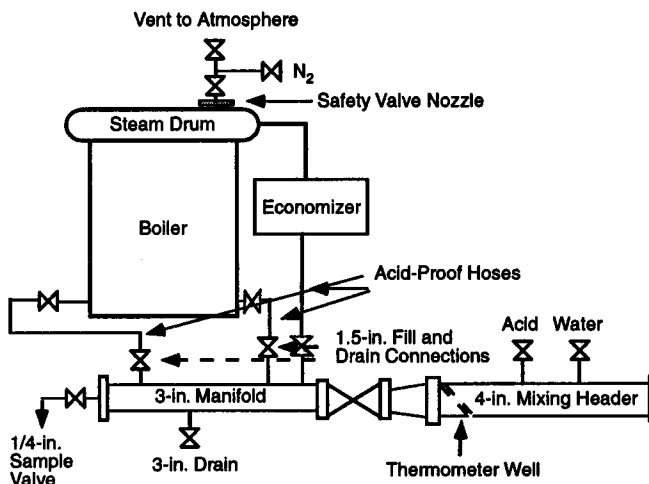


Figure 1. Setup for acid cleaning of a boiler with HCl.

cannot be used to remove deposits that contain calcium or barium because of the low solubility of CaSO_4 or BaSO_4 . Sulfuric acid can be used with several aldehydes^{20,21} to dissolve FeS without evolving hydrogen sulfide (see Chapter 5).

Nitric acid can be used to clean stainless steel (frequently with HF).²² Carbon steel corrosion is very difficult to inhibit (see Chapter IV) in this acid, because it is an oxidizing acid even at low (5%) concentrations.

Tanis²³ applied the mineral acid technology described above to boiler cleaning (see Figure 1). His suggested steps include (1) preparation, both solvent selection (acids or chelating agents) and the physical layout of the unit (see Figure 1); (2) temperature adjustment (to bring the boiler temperature to $<170^\circ\text{F}$, or $<77^\circ\text{C}$, for HCl); (3) an acid soak (usually lasts 6–8 h) in which the boiler is drained under nitrogen and then filled with a hot (150°F or 66°C) rinse of condensate grade water; and (4) after boil, in which a solution of soda ash and sodium phosphate is heated to $>212^\circ\text{F}$ ($>100^\circ\text{C}$) to neutralize any residual acid. Many boiler-cleaning sequences also include a passivation stage, using one of the solutions described in Chapter 4. Tanis also included sections on inspections and field analytical methods for following the course of the job. Several analytical tests were used to determine the concentration of iron as well as free (unspent) acid.

Chelating Agents and Organic Acids

Deposits that foul industrial equipment, such as boilers, steam generators, and heat exchangers, consist of oxides of iron, copper, nickel, and various metal salts such as calcium carbonate and calcium sulfate. Contacting the scale with a mineral acid such as hydrochloric acid can dissolve these deposits. Often, it is not desirable to contact the fouled metal with a strong mineral acid because of the danger of damage to the equipment during or after cleaning. An alternative solvent family consists of aqueous solutions of chelating agents and organic acids with pH values of about 2–12. A chelating agent is defined as a chemical that forms an equilibrium complex between the metal ion and the complexing agent. It is characterized by the formation of more than one bond between the metal and the molecule of the complexing

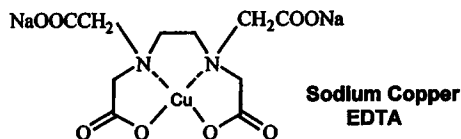


Figure 2. Chelate ring formation.

agent, and it results in the formation of a ring structure incorporating the metal ion (Figure 2).

This is contrasted with the reaction of a complexing agent such as ammonia or thiourea with a metal ion such as Cu^{2+} or Cu^+ , in which the complexing agent coordinates with only one reactive site on the metal ion. The formation of rings by the multidentate (many reactive sites) ligand gives added stability to the complex. The equilibrium for the reaction



does not go as far to the right for monodentate ligands as it does when a chelating agent is present. This is known as the “chelate effect.” The equilibrium constants for these reactions, $K = [ML_n]/[M][L]^n$, define the “strength” of the chelate complex. For example, the equilibrium constant for Cu^{2+} that reacts with four molecules of ammonia (NH_3) is 10^{13} ($\log K = 13$), while for the complex of Cu^{2+} with the chelating agent ethylenediaminetetra-acetic acid (EDTA), $\log K$ is 19 (Table 2).

Formulations containing chelating agents and organic acids were used to clean fouling deposits from metal for over 30 years. It is the objective of this section to review the published literature on the use of chelating agents and organic acids in chemical cleaning solvents. Included are formulations containing citric acid, EDTA, hydroxyethylethylenediaminetriacetic acid (HEDTA), phosphonates (see Figure 3 for structures), hydroxyacetic acid, formic acid, and other organic acid mixtures.

In 1958, Loucks et al.²⁴ described the use of citric acid as a cleaning agent. Reich²⁵ developed a formulation for removing iron oxide from steel surfaces that consisted of a mixture of citric acid and formic acid. He claimed that the mixture of the two acids would hold more iron in solution than either of the acids alone. Citric acid used alone precipitated iron after several hours of contact. A process for cleaning iron oxide and copper from utility boilers was described by Alfano.²⁶ This method uses monoammonium citrate at pH values between 3 and 5 to remove the iron oxide. The ammonium citrate solved the precipitation problems encountered with the use of citric acid alone. The pH is then raised to 9 with ammonia or an amine, and an oxidizer is introduced. The oxidizer dissolves the copper. The iron oxide removal stage is conducted at 150°F

TABLE 2

Stability ($\log K$ for 1 : 1 Complex) Constants of Chelating Agents

Ligand	Fe(II)	Fe(III)	Cu(II)
EDTA	14.3	25	18.8
HEDTA	12.2	29.8	17.5
DTPA	16.4	28.0	21.4
Citric Acid	4.4	11.5	5.9

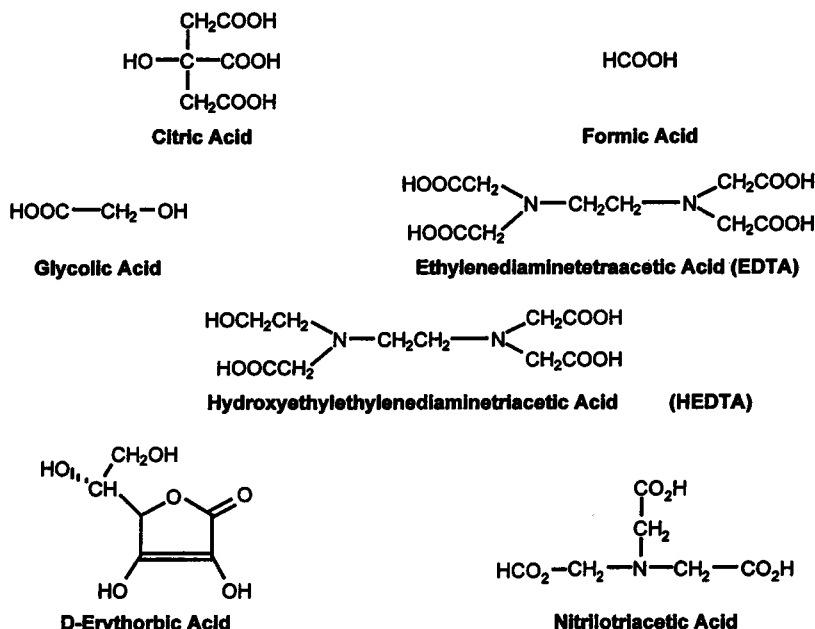


Figure 3. Organic acids and chelating agents.

(65°C) to 212°F (100°C), while the copper-removal stage is conducted at 150°F (65°C). The oxidizers include ammonium persulfate, potassium perchlorate, potassium bromate, sodium nitrite, potassium permanganate, and nitrophenyl sulfonic acid. Bell²⁷ also described a two-stage process for removing iron oxide and copper. The iron oxide stage is conducted at a neutral (7) pH, and the copper-removal stage is conducted at a pH of 9–10 by using an oxidizer.

A large boiler was cleaned²⁸ with the two-stage Alfano process, using 7500 lb (3375 kg) of citric acid, 3000 gal (11,355 L) of ammonium hydroxide, and an inhibitor. A total of 1560 lb (702 kg) of iron and 30 lb (13.5 kg) of copper were removed. The use of the corrosion inhibitor is significant because neither the Alfano nor Bell patents mention the use of an inhibitor. In fact, one advantage of the neutral-pH Bell process is lower corrosion rates than those found with low-pH ammonium citrate. A number of boiler tubes were cleaned in a lab loop.²⁹ Ammonium citrate was included. The major result was that ammonium citrate required a velocity of at least 1 ft/s (0.3 m/s) to adequately clean that boiler tube.

Sodium citrate at a pH of 4.0 was used to clean a service water system that was heavily scaled with iron oxide.³⁰ The authors described the dissolution of iron oxide with either ammonium or sodium citrate. A precipitate of ferrous citrate was noted at a low (3.5) pH, but this precipitate dissolved at higher pH values. A 65,000-gal (246,025-L) cooling water system was cleaned with 10% sodium citrate. Recently there have been additional investigations of the use of sodium citrate.

As noted above, citric acid was one of the first organic acids to be used in solvents to remove iron oxides from process equipment. While inhibited citric acid was used to clean various power-generating units in the 1950s, the formation of a gray precipitate also was noted. This problem is described in more detail, because it is a central issue when citric acid formulations are used in cleaning formulations. Morris³¹ described inconsistent laboratory experiments in which precipitates formed at iron

concentrations >1% and pH values from 4.0 to 4.85. However, he notes that many operational units had been cleaned without any evidence of a precipitate.

Morris speculated that the precipitate was a ferrous [Fe(II)] salt. Hamm et al.³² identified three Fe(II) complexes in aqueous solutions of citric acid and ferrous iron: FeHCit, FeCit⁻, and FeOHCit²⁻. Because FeHCit is the only identified uncharged species, the precipitate probably contained this compound. The aqueous chemistry of ferric/citric acid is more complex than the ferrous chemistry. The known Fe(III) complexes include FeHCit⁺, FeCit, FeOHCit⁻, and Fe(OH)₂Cit²⁻. In addition, Bobtelsky and Jordan³³ identified additional iron complexes (such as Fe₂Cit₃) in solutions containing sodium citrate and Fe(III). These authors also offer evidence that hydrated species may be present. One composition that solved the iron precipitate problem was patented by Reich.²⁵ He made mixtures of citric acid with formic acid that did not produce precipitates during the removal of mill scale from steel pipes.

Alfano and Bell^{26,27} devised a different resolution to the citrate precipitation problem. They developed solvents containing ammonium (approximately monoammonium) salts of citric acid, and they used them to remove iron oxides and copper from boilers. The mechanism proposed for the suppression of the precipitation of citrate salts included the formation of iron ammonium citrate complexes such as FeNH₄Cit and Fe(NH₄)₂OHCit. In addition, Bell³⁴ proposed that the formation of ferric ammonium citrate (FeNH₄Cit⁺) takes place during the Citro-Solv oxidation stage. Blume³⁵ also proposed that the addition of ammonia and the formation of ammonium ferrous citrate suppressed the formation of the insoluble ferrous acid citrate (FeHCit). An extensive review by Blair et al.³⁶ (with 112 references) reiterated the understanding developed concerning the use of citric acid, and it endorsed the use of the ammonium salts. Recently, Arrington and Bradley³⁷ analyzed the precipitate formed in citric acid solutions and stated that it consisted of FeHCit•H₂O, and that its formation was pH dependent. This observation led them to propose the use of sodium citrate (monosodium and disodium salts) as solvents for heavily scaled service water piping. A patent was also issued to Arrington³⁸ for the use of sodium citrate solutions to remove iron oxides from systems that have both iron-base and copper-base metals in the water circuit being cleaned.

Investigations in our laboratory corroborate Arrington's assertion that the complex that precipitates is the ferrous acid citrate species. The species that exist in solution as a function pH are shown in Figure 4. An insoluble FeHCit forms in the pH range of about 3.0 to 4.0. Raising the pH to >4 with either ammonia or sodium hydroxide eliminates this precipitate.

The EDTA is a very versatile chemical that forms metal ion complexes that have higher equilibrium constants than citric acid (Table 2). As a result, chemical cleaning solvents with pH values from 4.5 to about 9.2 have been formulated that are capable of removing Fe and Cu (as well as Ca, Ni, and Cr). A high pH iron oxide and passivating solvent was described by Lesinski.³⁹ Ammonium salts of alkylenepolyamine polyacetic acids (APAPA), and especially EDTA, were shown to dissolve iron oxides from steel at a pH of 9.0 and at temperatures up to 300°F (150°C), and would leave the steel in a passive condition (resists rusting). The copper in the scale is not removed by this process, but it can be dissolved by contacting the boiler surfaces with ferric EDTA produced by oxidizing the ferrous EDTA generated during the iron oxide dissolution process.⁴⁰ This copper removal stage is usually conducted at temperatures of 150–180°F (65–82°C). The ferric ion is generated by introducing an oxidizing agent

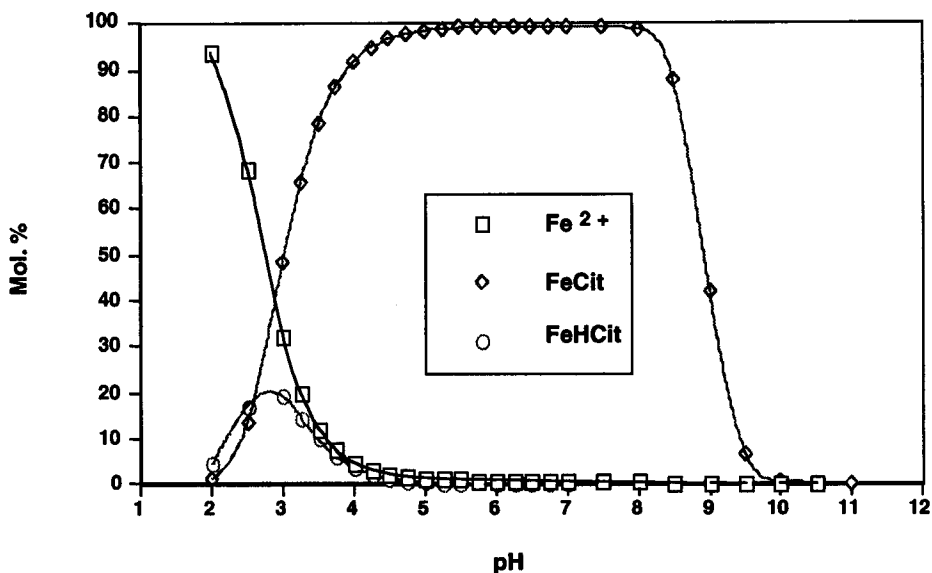


Figure 4. Ferrous/citric acid speciation (a 10% citric acid solution, equimolar iron).

such as air, sodium nitrite, hydrogen peroxide,⁴¹ or gaseous oxygen.⁴² The use of ammonium EDTA for dissolving iron oxide and copper from utility and industrial boilers was described by Slicker.⁴³ The mechanism of dissolution of magnetite in alkaline chelating agents was described by Frenier.⁴⁴ The iron oxide dissolves by a reductive dissolution mechanism:



The rate of the reaction depends roughly on the strength of the iron chelate for tests run on boiler tubes at a pH of 9.2 and a temperature of 325°F (163°C). The EDTA, diethylenetriaminepentaacetic acid (DTPA), and HEDTA all form strong chelate complexes with Fe(II), and they are much more aggressive solvents than nitrilotriacetic acid (NTA) and citric acid, which form much weaker complexes with iron. This study also showed that the magnetite must be electrically coupled to the steel for the kinetics to be favorable. The reductive dissolution of the base iron is driving the reaction. In addition, sodium chelates are not effective at a high pH because these salts do not have protons to satisfy Equation (9). However, sodium EDTA can be used to dissolve iron oxides at a pH of 4–5.⁴⁵ Also, Vinso⁴⁶ used sodium EDTA at a pH of 8–11 to remove hardness, then lowered the pH to 4–5 with acid, and used the same solution to dissolve iron oxides. More details about the dissolution mechanisms are contained in subsequent chapters.

If the boiler scale contains copper, a second copper-removal stage must be conducted that uses ferric EDTA as the oxidizing agent. Before the copper can be dissolved, the ferric EDTA must passivate the steel so that the copper will not replat. Frenier and Kennedy⁴⁷ described the conditions under which passivation is most readily achieved. These include high flow rates, high concentrations of ferric iron, and low temperatures. High concentrations of free chelant retards passivation. The study recommends using strong oxidizers such as air plus NaNO₂ or H₂O₂ to generate the ferric EDTA. The dissolution of copper itself was studied.⁴⁸ For EDTA, the ferric chelate dissolves the copper, while in citric acid, the external oxidizer (used to generate the

ferric chelate) dissolves the copper. The ferric EDTA is much more effective as a copper solvent than ammonium citrate with external oxidizers. This work also recommends using strong oxidizers (such as air plus NaNO_2 or H_2O_2) to generate the ferric chelate.

One advantage of the pH 9 ammonium EDTA solvent is that it can be used to clean natural circulation boilers, using thermal cycling to achieve flow in the tubes. Typically, at the start of a cycle, the steam drum temperature is about 260°F (127°C). By means of an igniter or some other auxiliary heat input, the temperature is raised to 300°F (150°C). By successive cooling and heating, the solvent is caused to flow and fresh chelant is brought in contact with the scale. Shorthouse⁴⁹ calculated that the flow in the tubes may vary from 0.19 to 1.3 ft/s (0.057–0.39 m/s) and recommends using more but smaller sources of thermal input, positioned as low as possible within the furnace to promote circulation.

A number of neutral-pH EDTA formulations were developed to dissolve magnetite (Fe_3O_4) found in nuclear steam generators. Pitzer⁵⁰ described a solvent that contains ammonium EDTA at a pH of 6.5–9 and from 0.1 to 0.5 M of hydrazine (N_2H_4). Magnetite is dissolved at 203°F (95°C) in the absence of a metal surface. The reductive dissolution apparently is provided by the hydrazine. Pocock and Leedy⁵¹ also developed a formulation of ammonia, EDTA, and hydrazine containing a corrosion inhibitor to remove magnetite from nuclear steam generators. The solvent was used at a pH of 7 and a temperature of 200°F (93°C). This mixture was much more effective than other solvents such as thioglycolic acid, citric/formic, ammoniated EDTA, or EDTA/citric acid. Additional testing of solvents for cleaning nuclear steam generators was conducted by Welty et al.,⁵² who tested 50 solvents for removing sludge (mostly magnetite, copper, and copper oxide) from the secondary side of steam generators. The solvent chosen for removing magnetite was pH 7 EDTA with hydrazine and an inhibitor. The copper solvent was 5% EDTA adjusted to a pH of 7 with ammonia, then to 10 with ethylenediamine, and containing 2% hydrogen peroxide as the oxidizer to dissolve the copper.

The EDTA formulations also can be used at temperatures of about 100–200°F (38–93°C) if the pH value has been adjusted to 4–5. The cleaning rate of magnetite from the boiler tube for tetra-ammonium EDTA and diammonium EDTA at two different temperatures is compared in Figure 5.

The HEDTA was tested as a solvent for iron oxides at a high pH,⁵³ and it is about as effective as EDTA. However, HEDTA acid has much higher solubility in water than EDTA acid (6% at room temperature vs. 0.1% for EDTA). Therefore, low-pH chelating solvents with exceptional iron oxide dissolution behaviors are possible.⁵⁴ Tests by Frenier⁵⁵ showed that formulations of HEDTA, HEDTA with formic acid, or HEDTA with H_2SO_4 will clean iron oxides from boiler tubing much faster than other acidic solvents such as hydroxyacetic/formic or diammonium EDTA. The increase in cleaning rate is attributed to the low pH (1.2–2.3) and the strong chelate bonds formed with Fe(III) even at a low pH. The removal rate of iron from a pipe scaled with red rust for two different solvents is compared in Figure 6. The low-pH solvent consisted of HEDTA/ H_2SO_4 , while the pH 5 solvent contained diammonium EDTA.

If the scale is mostly ferric oxide (FeOOH or red “rust”), a safe solvent⁵⁶ using HEDTA and the reducing agent erythorbic acid can be used to clean cooling water systems at temperatures at or below 150°F (65°C).

Phosphonates are chemicals that are analogs to carboxylic acids in which the carboxylate group is replaced with $-\text{PO}_3\text{H}_2$. They form chelate complexes that are

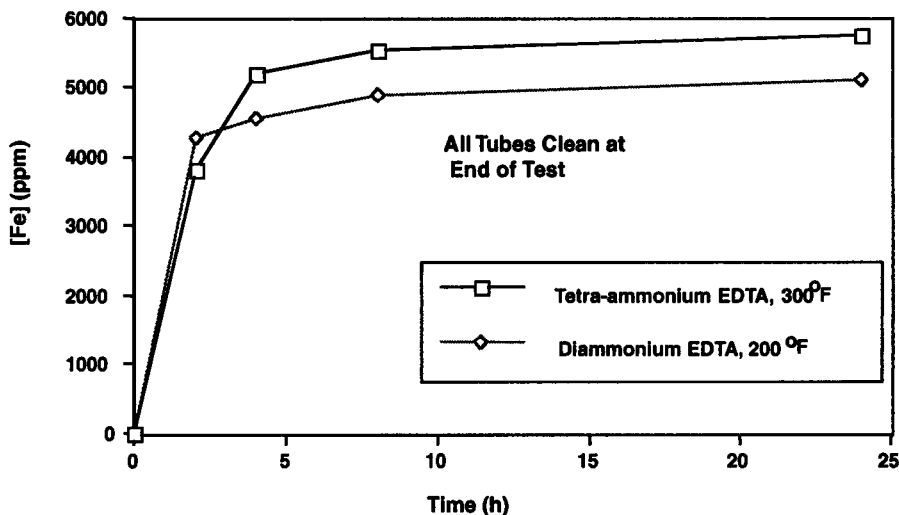


Figure 5. Cleaning of boiler tubes in stirred bombs. All Contain 0.25% inhibitor.

similar to the aminocarboxylic acids and were proposed as cleaning compositions. Frost et al.⁵⁷ described solutions for dissolving magnetite and copper that consist of 1-hydroxyethylidene-1,1-diphosphonic acid, *N, N, N', N'*-ethylenediaminetetra-(methylenephosphonic acid), or nitrilotri-(methylenephosphonic acid), brought to a pH of 9 with ammonium hydroxide. The phosphonic acids are used at temperatures above 180°F (82°C) to dissolve magnetite from boiler tubes. The iron solutions formed from the dissolution of magnetite are used with oxidizing agents such as NaNO₂, NaBrO₃, or H₂O₂ to remove copper. Descaling formulations of aliphatic phosphonates and nitrates were described by Halsey.⁵⁸ His patent claims that the solution of the aliphatic phosphonate and ammonium nitrate at a pH of 8.0 removed magnetite and copper oxide from a boiler tube at 208°F (98°C). Mixtures of aminopolycarboxylic acids and aminotrimethylenephosphonic acids (AMTP) are reported to be superior to either chelating agent used alone. Arrington and Bradley⁵⁹ tested mixtures of NTA and AMTP for dissolving magnetite from a boiler tube with added copper. The pH 9

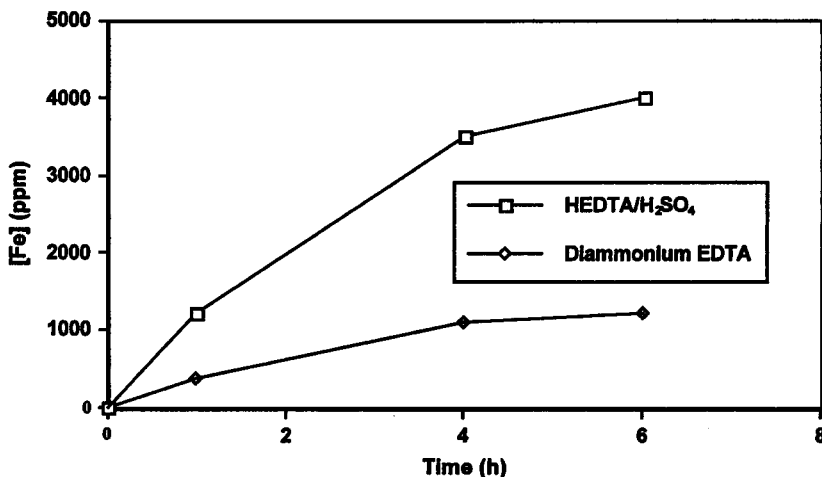


Figure 6. Cleaning of water piping at 100°F (38°C).

formulation was heated at 275°F (135°C) to dissolve the iron oxide, then cooled to 150°F (65°C), and oxidized with air and NaNO₂ to dissolve the copper. The data showed that the mixture removed the deposits better than NTA alone, and did not produce any undesirable precipitates that may be formed if the phosphonates are used alone.

All of the chelating agents described above also are organic acids. This section includes a review of the use of organic acid solvents that are not primarily chelating agents, or solvents in which the chelating agent component is a secondary constituent. Eberhard and Rosene⁶⁰ claimed the use of solvents consisting of formic acid or citric acid for cleaning nondrainable tubes in superheaters and reheaters. The solvent (5% or 10%) also included a corrosion inhibitor. Reich²⁵ developed a solvent that contained from 3/1 to 1/6 weight ratio of formic acid to citric acid as a solvent for removing iron oxide deposits. The advantage of these mixtures was that the acid mixtures avoided the precipitation of solids that formed in pure formic or citric acid solutions.

Other mixtures of organic acids were investigated by McLaughlin.⁶¹ He produced mixtures of formic acid with hydroxyacetic acid (HA) and formic acid, and citric acid mixed with hydroxyacetic acid. He found that a mixture of HA with formic acid at a 2/1 ratio held more iron in solution than other mixtures. This work yielded the "HYFor" mixtures that are currently the standard solvents for cleaning once-through boilers.

Frenier and Larson⁶² proposed a solvent that is predominantly formic acid and also contains iron stabilizers and corrosion inhibitors. This mixture was developed for cleaning once-through (OT) boilers. A dynamic loop (Figure 7) was constructed to

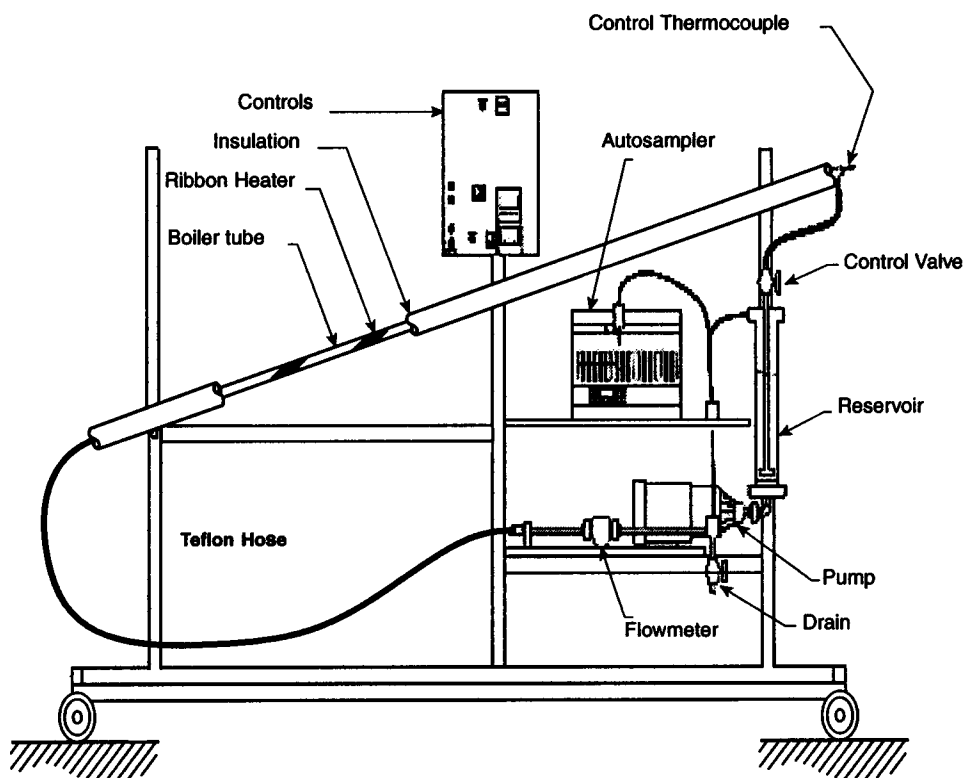


Figure 7. Test loop.

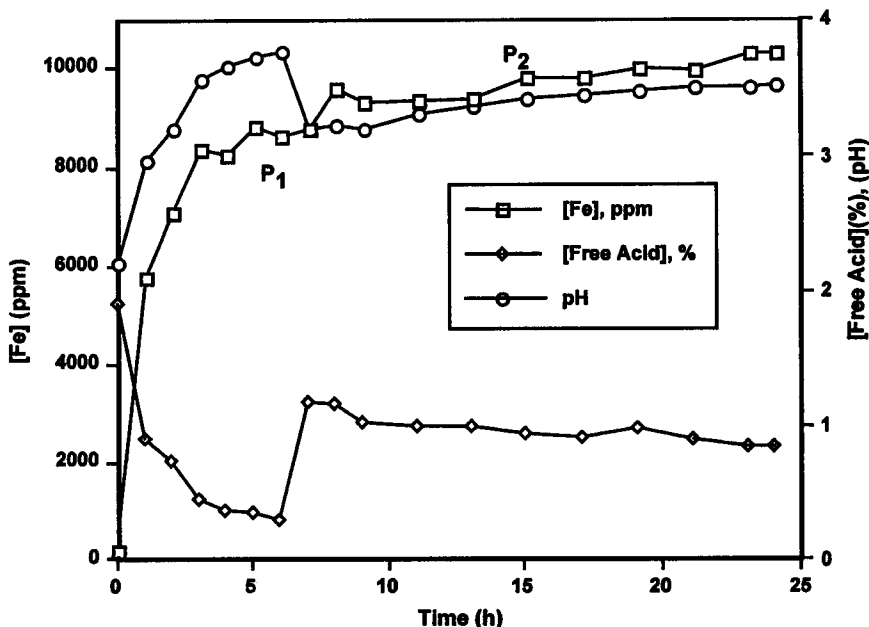


Figure 8. Cleaning profile of V516 fluid at 200°F (93°C).

compare the new solvent with HYFor. The loop uses a 10-ft (3-m) section of boiler tubing as the heat exchanger and matches the surface/volume ratio and flow rates observed during cleaning of the once-through type of boiler. Oxide dissolution curves developed using the loop demonstrate that the new solvent cleaned the tubes almost as fast at 150°F (66°C) as HYFor when used at 200°F (93°C). The kinetic profile for the operational cleaning of a 25,000-gal (94,625-L) OT boiler using this solvent (organic acid fluid, V516) is shown in Figure 8. The unit was cleaned in less than 24 h despite scale loading that approached 80 g/ft² (888 g/m²).

Poulos⁶³ described a study that compared ammonium citrate with several organic acid solvents. In this test, loose magnetite was dissolved in the solvents. Monoammonium citrate or EDTA solvents were much more effective than the organic acids (including HYFor). Because reductive dissolution mechanisms were not active, his conclusions are valid. However, when magnetite is deposited on carbon or alloy steel, reductive dissolution yields ferrous ions, which are very soluble in the organic acids. Frenier and Larson⁶² noted that loose magnetite dissolved much slower in the V516 solvent than the magnetite on the tube surfaces.

A mixture of citric acid and gluconic acid that contains ammonia and a corrosion inhibitor was claimed by Veysset and Saurin⁶⁴ as a solvent for removing sludge (iron oxide and copper) from PWR (Pressurized Water Reactor) steam generators. The oxide dissolution is conducted at a pH of 3–3.5 and a temperature of 176°F (80°C). The copper removal stage is run at a pH of 9.5 and a temperature of 122°F (50°C). Hydrogen peroxide is added to improve copper dissolution. This process is claimed to be as effective as the EPRI/SGOG (Electric Power Research Institute/Steam Generators Owners Group) process that used EDTA. Additional mechanistic details of iron oxide and copper removal are contained in subsequent chapters.

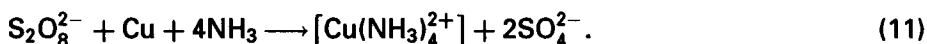
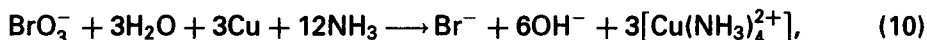
Additional organic acid formulations also have been proposed. Horner⁶⁵ described the use of citric acid, tartaric acid, and gluconic acid in abrasive polishing and

electropolishing of metals. Gluconic acid appears in several complex metal cleaning formulations.^{66,67} This acid will complex and prevent the precipitation of iron during cleaning operations. Kaplan⁶⁸ claimed that iron oxide deposits found on heat transfer surfaces can be removed by using a mixture of tannin (sumach, valonea, or chestnut) followed by a dilute solution of citric acid. Cooling water systems were cleaned by using this process.

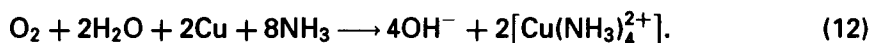
SOLVENTS FOR REMOVING COPPER DEPOSITS

Copper-containing deposits may be found in process equipment any time that the fluids come in contact with copper-base alloys. While most copper alloys are relatively resistant to corrosion, very small amounts of copper will dissolve, and then may replate on contact with an iron-base alloy. Copper that is plated onto the steel will accelerate corrosion because of the galvanic nature of the iron/copper couple. The copper acts as the cathode for the oxidizing agent, while the anodic iron corrodes. Many different techniques have been developed for removing copper deposits. Included are sections on alkaline oxidizers, HCl/complexers, and chelating agent solvents.

As noted in the Nesbitt⁶⁹ review, early use of alkaline inorganic oxidizers included several ammonical solutions such as ammonium persulfate (in 1948) and ammonium bromate (in 1951). Alquist et al.⁷⁰ claimed a number of ammonical oxidizers for cleaning steam generators. A bromate solvent was developed that consisted of sodium bromate, ammonium hydroxide, and ammonium bicarbonate, and it was used at 120–175°F (49–79°C). It is effective, but ammonium bromate can form a very explosive mixture under some circumstances. Hydrogen peroxide also will cause rapid (explosive) reactions with concentrated organic materials, including EDTA. The bromate reaction is seen as Equation (10), and the ammonium persulfate reaction is seen as Equation (11):



An important improvement is embodied in the copper-removal technology using ammonium carbonate and oxygen that is protected by a U.S. patent.⁷¹ This process uses ammonium bicarbonate, aqua ammonia, and gaseous oxygen to dissolve complex copper and thus remove it from surfaces. The oxidation reaction is Equation (12):



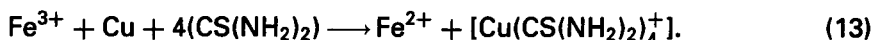
Because the oxidizer can be continually replenished by introducing more oxygen, very large amounts of copper may be removed from boilers and other copper-fouled equipment. The spent solution also does not have to be reduced prior to waste treatment. An additional oxidizing agent claimed for use in removing copper is sodium perborate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$), which can be used with ammonia, amines, or with EDTA.⁷² The alkaline oxidizers containing ammonia passivate the steel as the copper is being dissolved. This passivation process prevents the copper from replating onto the steel. The redox reactions and their half-cell potentials are seen in Table 3.

The alkaline oxidizers described above could remove copper deposits, but they had to be staged with mineral acid, usually inhibited hydrochloric acid (HCl), to

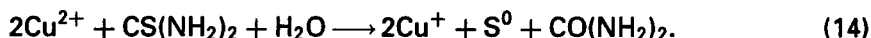
TABLE 3
Redox Reactions

Half-Cell Reaction	Standard Potential (V)
$\text{Cu}^{2+} + 2\text{e} = \text{Cu}$	0.34
$\text{Cu}^+ + \text{e} = \text{Cu}$	0.52
$2\text{H}^+ + 2\text{e} = \text{H}_2$	0.00
$\text{BrO}_3^- + 3\text{H}_2\text{O} + 6\text{e} = \text{Br}^- + 6\text{OH}^-$	0.61
$\text{Fe}^{3+} + \text{e} = \text{Fe}^{2+}$	0.77
$\text{Fe(III)EDTA}^- + \text{e} = \text{Fe(II)EDTA}^{2-}$	
$\text{Fe} = \text{Fe}^{2+} + 2\text{e}$	0.45
$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e} = 3\text{OH}^-$	0.88
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} = 4\text{OH}^-$	0.40
$2\text{NO}_2^- + 3\text{H}_2\text{O} + 4\text{e} = \text{N}_2\text{O} + 2\text{OH}^-$	0.15
$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e} = \text{NO}_2^- + 2\text{OH}^-$	0.01

remove iron oxide deposits containing copper or copper oxides. This resulted in use of acid/bromate stages or bromate/acid/bromate stages for very heavy copper-containing scales. Additional research yielded the acid/thiourea cleaning process.⁷³ This procedure (and a procedure using sulfuric acid and allylthiourea) allowed the cleaning industry to simultaneously remove iron oxides and copper deposits from utility power boilers. This dual process reduced the number of stages required to clean a boiler (and thus the amount of waste solvent). The major problem was that the amounts of thiourea required (per pound of copper) *decreases* as the concentration of copper increased. For boilers with a small amount of copper, a considerable excess concentration of thiourea is required to prevent a precipitate from forming, especially with localized deposits. It is important to note that the ferric ions generated during the dissolution of the magnetite oxidize the copper and allow the thiourea to complex it. This process will not dissolve any plated copper that is not oxidized by the ferric in the scale. See Equation (13):



In addition, McCoy⁷⁴ proposed that thiourea may reduce any 2+ oxidation state copper to the 1+ oxidation state:



Improvements in the acid/thiourea process resulted from the discovery that thiourea mixed with other thiourea derivatives [hexahydropyrimidine-2-thione, *N*-(hydroxyethyl)-ethylthiourea] produced formulations⁷⁵⁻⁷⁷ that were more resistant to formation of precipitates than thiourea itself. These patents claim that the precipitate formed in the presence of the mixed complexer is more “flocculent in nature” than the precipitate formed with thiourea, and thus is easier to flush out of the boiler than the other material. See Figure 9 for some of the chemical structures.

Polarographic methods were used by Frost et al.⁷⁸ to determine the cumulative stability constants (β ; four ligands would be represented as β_4) of substituted thiourea derivatives with Cu(I) in acid. Values for β_4 that were greater than 10^{15} were determined for thiourea, hexahydropyrimidine-2-thione, and several other complexes with Cu(I). These very high stability coefficients in acid explain the ability of these ligands to prevent copper from plating onto steel in HCl at acid concentrations >1 M.

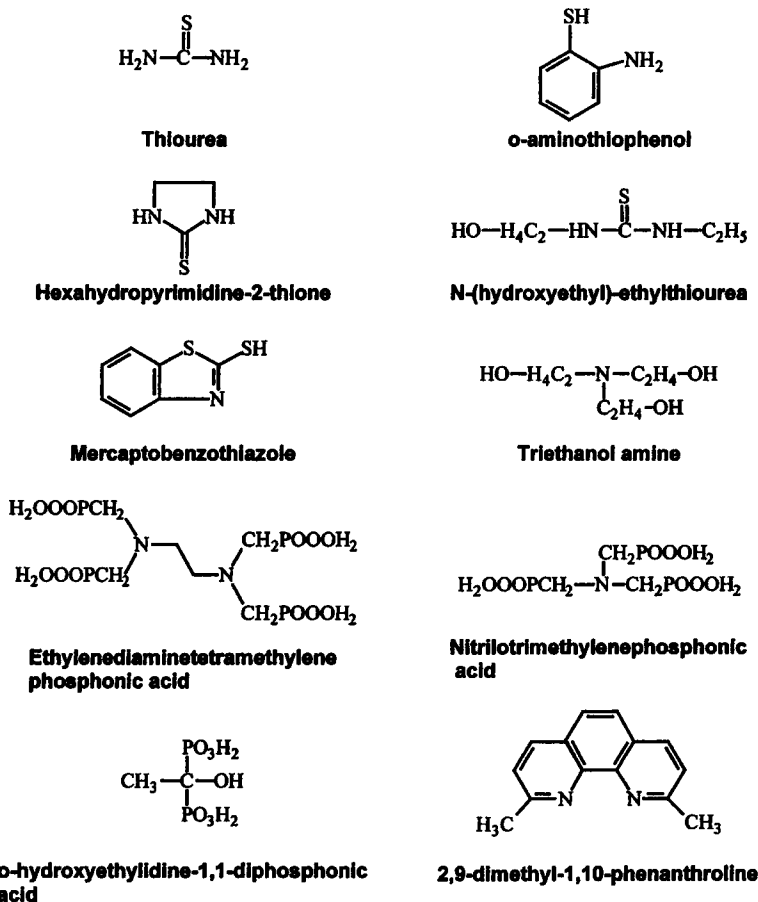


Figure 9. Copper ligands.

The only other complexer claimed to be of use for removing copper in HCl was a substituted o-aminothiophenol.⁷⁹ They claimed that these acid solutions dissolve more scale than acid/thiourea. However, this author does not think that these formulations were commercially used to clean boilers. Thompson⁸⁰ claimed an inhibitor mixture to prevent replating of copper from cleaning solutions containing HCl. The mixture included bis(hydroxyethyl) aminomethyloctyl sulfide and a polyethylene glycol surfactant.

The use of ammoniated citric acid solutions to dissolve iron oxide deposits, and the use of the same fill of solvent to dissolve copper, was developed by Alfano²⁶ and Bell.²⁷ This technology led to the development of the Citro-Solv processes. The chemistry involves the use of inhibited ammonium citrate (pH of 3.5–5.0) to dissolve iron oxides from steel surfaces. The iron-spent solvent is cooled (from about 200°F or 93°C to about 150°F or 66°C), additional ammonia is added to elevate the pH to 9 to 10, and an oxidizer (air and/or sodium nitrite) is added to dissolve the copper, which is then complexed by the ammonia as $(\text{NH}_3)_4\text{Cu}(\text{II})$. During this oxidation process, the ferrous citrate generated during the iron oxide stage becomes oxidized to ferric citrate. Frenier and Kennedy⁴⁸ demonstrated that the dissolved oxygen and sodium nitrite are the primary oxidizing agents for the plated copper; see Equations (15) and (16). This is contrasted with EDTA base iron/copper solvents (discussed in the next

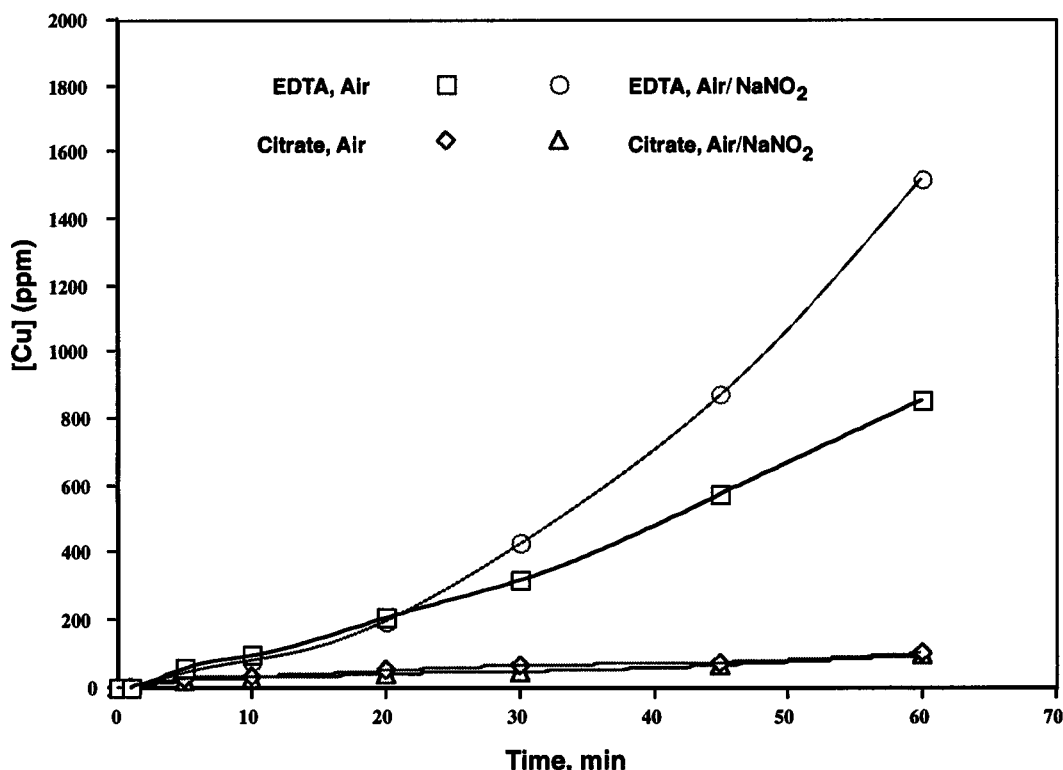
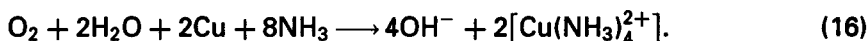
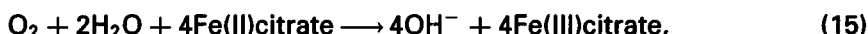


Figure 10. Dissolution of copper from plated steel in Fe(II) chelate, 7000 ppm of Fe, at 150°F (66°C).

section), in which the oxidized iron reacts with the copper and the external oxidant acts to generate the ferric EDTA. Because the concentration of iron(III) EDTA is much higher than dissolved oxygen (7000 ppm vs. about 8 ppm), the EDTA/iron solution dissolved copper much faster than citric/iron solutions. See Figure 10 for relative dissolution rates of copper in EDTA and citric acid solutions.



The original Citro-Solv process was used at temperatures of about 200°F (93°C) for the iron stage and at about 150°F (66°C) for the copper stage. Recent improvements have included the use of ammonium bifluoride to speed the rate of iron oxide removal, and the use of higher temperatures, that is, up to 300°F (149°C). The increased temperatures require that the iron stage is conducted at a pH of 6.0, so that the inhibitors can adequately control the corrosion rate of the metal being cleaned. Additional variations include the use of triethanolamine (TEA—instead of ammonia) for primary pH control.⁸² This variation improves the safety of the solvent used (TEA is less toxic than ammonia), and it also reduces the cracking incidents of copper-base metals in mixed metal systems (ferrous and copper).

Work by Lesinski³⁹ resulted in the development of an ammonium EDTA-base solvent (tetra-ammonium EDTA) for dissolving magnetite (Fe₃O₄) from utility boilers. However, copper dissolved (as a result of the ferric ions in the scale) and then re-plated onto the boiler surfaces. There were several attempts to prevent the replating of

copper and an “air-blowing” process was developed. It also was realized that production of a “protective passive film” would enable the copper to remain in solution after the ferric EDTA dissolved it. The ideas of passivation as well as copper removal were incorporated into the patents that were issued to cover this technology.^{83,84}

In the commercially developed process (called the alkaline copper-removal process), the ferrous EDTA generated during the dissolution of magnetite is oxidized by air (sometimes containing sodium nitrite). The oxidized chelating agent (ferric EDTA) passivates the steel and then oxidizes the plated copper. Passivation of the steel is a critical part of the process and was monitored indirectly by measuring the electromotive force (emf) of the solution. Frenier and Kennedy⁴⁷ demonstrated that the solution potential reflects the ratio of [Fe(II)]/Fe(III)] and not the real passivation potential of the surface. However, when the emf solution is in the range specified by the patents, the surfaces usually have become passive. The passivation is caused by the strong oxidizer, Fe(III)EDTA, diffusing to the surface and raising the surface emf into the passive region. See Chapter 4 for details of this process.

The actual removal of copper is accomplished by oxidation of the plated metal by the ferric EDTA:



This is contrasted with the situation when ammonium citrate is used and the external oxidizer removes the copper (see the discussion in previous section). The continuing “air blowing” keeps the iron in the ferric oxidation state and also provides some of the motive force to the solvent that speeds passivation and copper dissolution.

Additional improvements in the copper-removal technology in EDTA included the use of H_2O_2 as the oxidant during the copper stage.⁴¹ Use of this chemical can substantially increase the rate at which the ferric EDTA is generated. The time to achieve passivation is shortened and copper removal is enhanced. In a similar manner, use of air/ NaNO_2 and gaseous oxygen⁴² enhances passivation of the boiler metal, speeds conversion of ferrous EDTA to ferric EDTA, and thus increases the rate of copper dissolution. With the use of the oxygen or the hydrogen peroxide methods, copper removal can be accomplished in as little as 2 h. The oxygen process is preferred when there is little external circulation. In these situations, the high concentration of hydrogen peroxide may cause the chelant to degrade, or the iron salts may decompose the peroxide.

Several additional formulations with EDTA (or citric acid) and other materials have been proposed. Martin⁸⁵ patented a mixture of hydrogen peroxide, oxalic acid, and an EDTA or citric acid-type complexer for removing copper deposits (iron oxides are removed by using an additional stage). An unusual aspect of this process is that it is performed at a pH of 3.0–6.0. To allow passivation of the steel to be effective, oxidative copper-removal processes usually are conducted at pH values of >9.0.

A successful commercial process for removing copper from steel was developed by Jevac and Leedy⁸⁶ and Cleary and Gockley.⁸⁷ This process uses 5% EDTA, 2% H_2O_2 , ammonia to raise the pH to 7.0, and then ethylenediamine to raise the pH to 10.0. This formulation is used after the EDTA/hydrazine iron oxide stage in the EPRI/SGOG process for removing iron oxide and copper from utility boilers. This procedure was successfully used to dissolve copper during the cleaning of nuclear steam generators.

While it is an effective process, the large amount of steel, Inconel, and sludge causes much of the hydrogen peroxide to decompose by an auto redox reaction:



After the peroxide decomposes, the solvent's capacity for dissolving copper is greatly diminished. This references noted above (86, 87) contains many examples of solvents that led to the final development of this process. The high concentrations of peroxide needed for this process also may cause the EDTA to be degraded. This reaction is known as the Fenton chemistry, and the active oxidant probably is the hydroxyl radical, $\bullet\text{OH}$. See the discussion of chelate degradation by Chen et al.⁸⁸

A dual-stage system using polyphosphonic acids, such as nitrilotrimethylene-phosphonic acid and ortho-hydroxyethylidene-1,1-diphosphonic acid,⁵⁷ used the ammonia or amine salts to dissolve iron oxides. The same solutions are oxidized by using hydrogen peroxide, sodium bromate, or sodium nitrite to dissolve copper. The technology is similar in concept to the EDTA-based technology described above. Precipitation of ferrous/phosphate containing solids is prevented by the addition of ammonium bifluoride.⁸⁹

SOLVENTS FOR CALCIUM AND BARIUM DEPOSITS

Solutions of sodium EDTA can be used to dissolve deposits containing calcium sulfate or calcium carbonate. In fact, the removal of calcium was one of the first procedures performed by using EDTA formulations. Bersworth⁹⁰ claimed the use of alkali metal (sodium or potassium) salts of EDTA for removing hardness deposits from boilers. The pH was >8 , and the temperature was at about the boiling point of water. He even developed a method for regenerating the EDTA used to dissolve calcium salts by adding sulfuric acid to precipitate calcium sulfate. The pH is then elevated to the use level (12) with sodium hydroxide. A reactive scale removal formulation was invented by Quattrini.⁹¹ The solvent contained a neutralized (pH of about 6.5) EDTA solution and ammonium carbonate to remove gypsum (a form of calcium sulfate) from heat exchangers and oil wells. Hayashi⁹² cleaned well tubing at a geothermal plant by using a pH 6 solution of potassium EDTA. The treatment temperature was up to 400°F (200°C), but this solvent was a factor of 10 less corrosive than inhibited HCl to the well tubing (steel). Also, Visno⁶⁴ used sodium EDTA at a pH of 8–11 to remove hardness, then lowered the pH to 4–5 with acid, and used the same solution to dissolve iron oxides.

Barium-containing scales are more difficult to remove than calcium-containing scales because the kinetics of the dissolution reactions are much slower than the calcium scales. There has been considerable interest in removing BaSO_4 scales from (oil and gas well) tubulars and from the near wellbore region. Conventional chelant solvents have slow reaction rates with these scales. An additional concern with the barium sulfate deposits is the occurrence of naturally occurring radioactive material (NORM) in conjunction with the sulfate scales. Paul^{93–95} has proposed several solvents for the sulfate scales that are based on the use of a scale "converter" or dissolution catalysts with a chelating agent. The chelate can be EDTA based, but DTPA is more effective in this formulation. Oxalic acid, fluoride, and dithionate are described as being catalysts. The basic idea is that the converter or catalyst reacts at the surface of the scale and "converts" the deposit to a more soluble form that the chelate can then complex.

CONCLUSIONS

The past 30 years could be called the “era of EDTA.” This chemical dominated technological developments and enabled power boilers to be cleaned with fewer fills of solvent than was possible by using mineral acids. This material (or similar molecules) is also being used in formulations to dissolve barium and calcium scales from downhole and process tubing. However, EDTA caused chemists and engineers to develop complicated and expensive technology (described in Chapter 6) to remove the metals from the cleaning solvents prior to disposal. In addition, EDTA is not biodegradable, so the ultimate fate of the chemical in the environment is not known. Recently, there has been an increased interest in the use of biodegradable chelating agents such as citric acid, even though these formulations may not be as effective as EDTA solvents. Clearly, new molecules are needed.

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3

MECHANISMS OF IRON OXIDE AND COPPER DISSOLUTION

Research into methods to remove iron oxide and copper deposits from power-generating equipment constitutes a large portion of the activities of laboratories involved in chemical cleaning operations. With the exception of the work on corrosion inhibitor mechanisms, there is more published information on the chemistry of iron and copper removal than other techniques. A separate chapter is devoted to a review of this information.

IRON OXIDE DISSOLUTION MECHANISMS

The chemical dissolution of iron oxide deposits involves many processes that are designed to enhance the service life of steel industrial equipment (such as heat exchangers, boilers, and steam generators). Deposit removal improves heat transfer and reduces pitting corrosion. Our knowledge of the stability and dissolution of iron oxides directly affects these processes. Diggle¹ reviewed the subject of iron oxide removal from oxide surfaces in 1973; emphasis was placed on the electrochemistry of the processes involved. Over the past few years, removal of scale (oxide on a metal surface) began to receive scientific attention. In addition, the study of well-defined systems was perceived to be even more necessary for the understanding of the dissolution process; much of the work in this area focused on the dissolution of powdered magnetite.

The purpose of this section is to review recent literature on the kinetics and mechanisms of iron oxide dissolution. Particular emphasis is placed on pure iron oxides and iron oxides on steel surfaces. The limited scope of this review precludes complete coverage of the vast amount of work on passive film formation and dissolution. However, some aspects of passivation that apply directly to chemical cleaning are reviewed in Chapter 4.

Electrochemistry

The studies of Vermilyea² and Engell³ provided some of the earliest theoretical bases for the dissolution of iron oxides. Vermilyea expressed the rate of oxide

dissolution as

$$r = \frac{2r_f}{\exp(\alpha^- z^- F\eta/RT) + \exp(\alpha^+ z^+ F\eta/RT)}, \quad (1)$$

where r_f is the rate of the freely dissolving crystal, η is the applied overpotential, α designates the transfer coefficients of the ions, and z designates the ionic charges. The discussion is concerned only with changes in the overpotential at the double layer, and Vermilyea states that a doubling of the dissolution rate is the maximum rate change achievable, regardless of η . The driving force for oxide dissolution is the potential difference across the Helmholtz layer:

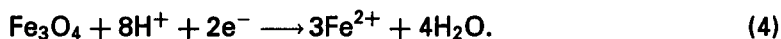
$$\phi_s - \phi_{ohp} = (RT/ZF) \ln(a/a_0), \quad (2)$$

where ϕ_s and ϕ_{ohp} are the potentials at the surface and outer Helmholtz plane, a is the activity of the potential determining ion, and a_0 is its activity at the zero charge potential (ZCP). In the absence of interfering ions, the proton (H^+) is the potential determining ion. Thus, pH controls the dissolution rate.

Other electrochemical phenomena must also be considered when the oxide is on an iron surface. Most authors agree that iron is released from the oxide only as the ferrous (Fe^{2+}) ion. Hickling and Ives⁴ stated that an Fe^{3+}/Fe^{2+} redox system in the solid state is established and produces a potential determining exchange current. Therefore,

$$E = E' - 0.059 \text{ pH} - 0.059 \log[aFe^{3+}(\text{soln})]. \quad (3)$$

Haruyama and Masamura⁵ stated that the reductive dissolution of magnetite occurs with 100% efficiency in the potential range from 0–900 mV (vs. SHE), as follows:



While there is some disagreement about the effect of potential, these authors and others^{5,6} agreed that the cathodic current is essential and that the rate-determining step is the transfer of the Fe^{2+} and O^{2-} (or OH^-) ions across the interface; that is,



and



or



or



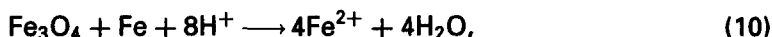
Haruyama and Masamura⁵ concluded that the overpotential changes the magnetite by a transfer of ions across the interface until the chemical potential of the potential determining ions (Fe^{2+}) balances the overpotential:

$$\eta = E = E_0 - 0.059 \log[Fe^{2+}]/[Fe^{3+}]. \quad (9)$$

However, Diggle¹ discounted the possibility of the dissolved iron (Fe^{2+}) being the potential determining ion.

An interesting observation of Hickling and Ives⁴ is that the redox potential of dissolving magnetite and the Flade potential (the potential at which the passive film dissolves) in a similar solution are almost identical, implying that passivation and dissolution of oxides are simply reversible reactions of the same type. A similar observation by Allen et al.⁷ supports this idea. In contrast, there is evidence that the passive film on iron is composed primarily of a highly protonated, trivalent iron oxyhydroxide.⁸

Shoesmith et al.⁹ has made an extensive study of oxide-covered iron electrodes in EDTA and citric acid solutions. Three distinct potential regions were observed. In Region I ($E > -100$ mV vs. SCE), little Fe^{2+} was released, and there was only minor oxide dissolution. This is considered the induction period for pore formation. In Region II (-450 mV $< E < -100$ mV), potential values were between those of magnetite reduction (reductive dissolution) and metal dissolution, suggesting that auto-reduction,



was proceeding. The rate of Fe^{2+} release increased with negative potential changes in agreement with Equations (1) and (2). At potentials more negative than -450 mV, H_2 evolution predominated, and oxide dissolution ceased. Two electrochemical studies of iron oxide in EDTA solutions by Brunet and Turluer¹⁰ and Brunet et al.¹¹ and also confirmed reductive dissolution of Fe_3O_4 from steel surfaces. Ogura and Sato¹² and Ogura and Ohama¹³ showed that cathodic reduction of iron oxides on iron is drastically affected by chelating agents such as glycine, NTA, EDTA, and iminodiacetic acid; this probably is the result of a shift in $\alpha\text{Fe}^{2+}/\alpha\text{Fe}^{3+}$ caused by the preferential formation of Fe(II) or Fe(III) complexes.

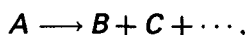
Both magnetite dissolution and dissolution of the base metal contribute Fe^{2+} to the solution. Separating the two contributions is at best a difficult procedure. Most of that effort focused on the dissolution rate of the base metal through a passive film.^{14,15} The rate of that process appears to depend on the ratio of film thickness, L , to the metal/solution potential difference, ϕ_M . The dissolution process implies transfer of metal ions to the oxide phase, followed by ion diffusion through the oxide, transfer through the oxide solution interface, and finally hydration of the ions. Thus, the potential difference at the Helmholtz layer is given by

$$\phi_H = \phi_M / (1 + L\varepsilon_H / S\varepsilon_F), \quad (11)$$

where S is the thickness of the Helmholtz layer, and ε_H and ε_F are the dielectric constants of the Helmholtz and oxide layers, respectively.

Reaction Kinetics

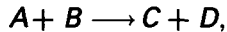
The dissolution of powdered magnetite of a particle size < 100 μm in HCl , H_2SO_4 , H_3PO_4 , and Na_2EDTA at 68 – 176°F (20 – 80°C) was investigated by Gorichev et al.^{16–20} Reaction rate curves—fractional conversion, α , vs. time—were S-shaped (sigmoidal) in all cases. The rate curves for hematite and wustite, in contrast, lacked the initial “induction period” observed with magnetite. Sigmoidal curves are typical of second-order autocatalytic reactions²¹ of the type



where the rate of loss of A can be expressed by

$$d\alpha/dt = k\alpha(1 - \alpha). \quad (12)$$

Reactions that are catalyzed by a product can often be treated with Equation (12). Many growth²² and decay²³ processes also give sigmoidal curves. Higher-order autocatalytic reactions may likewise be fitted into this scheme. For reactions of the type



where C catalyzes the reaction, the rate at which A is lost can be expressed by

$$d\alpha/dt = k\alpha^p(1 - \alpha)^q a_B^r. \quad (13)$$

Here p , q , and r depend on the elementary steps in the mechanism, and α is the activity of reactant B . The rate curves for hematite and wustite can be treated by the simple m th-order rate expression,

$$d\alpha/dt = k\alpha^m, \quad (14)$$

where $m \sim 1$.

Gorichev et al. found that their dissolution data for Fe_3O_4 fit the following equation developed by Tanaka and Tamamushi²⁴ for localized corrosion, or etching:

$$-\ln(1 - \alpha) = A \sinh(kt). \quad (15)$$

The model assumes that the rate is controlled by the formation (nucleation) and growth in one dimension (filaments) of a solid intermediate.^{16,25} The total rate of filament growth is a function of the rate of nuclei formation. The rate expression from which Equation (15) was obtained can be approximated by

$$d\alpha/dt = k\alpha^m(1 - \alpha), \quad (16)$$

which, it will be noted, is a special version of Equation (13).

A variety of rate laws in addition to Equation (16)—and its integrated form, Equation (15)—were examined, but these were less successful at fitting the data for magnetite dissolution. Most notable of these is the Erofeev relation,²² which like the Tanaka expression was developed to treat solid-state decomposition reactions in which a solid product phase is formed. This has the form

$$-\ln(1 - \alpha) = kt^j. \quad (17)$$

In one scenario,¹⁸ the dissolution of magnetite entails formation of an unstable iron-deficient oxide phase produced by the more rapid migration of iron ions out of the oxide matrix; the reaction rate is governed by decomposition of this peroxide-like species. Gorichev et al.¹⁸ determined a value for j of 2.2 ± 0.2 in H_2SO_4 , but it was apparent that the fit of the data was poor. The Erofeev reaction does not appear to be suitable for the treatment of data prior to the induction period.

Reaction Kinetics in Acid

Azuma and Kametani²⁶ performed a series of experiments on the dissolution of ferric oxides in mineral acids. S-shaped curves similar to those of Gorichev et al. were found. They treated their data with the expression

$$\log W = \log C + j \log t, \quad (18)$$

in which W is the weight percent oxide dissolved at time t and C is a rate constant. This rate law is actually the same as the Erofeev relation, Equation (17).

In a different study, Gorichev et al.¹⁸ found that the dissolution rates of wustite, hematite, and magnetite in EDTA all peaked at a value of 0.5–0.6; see Equation (15). In the mineral acids, magnetite gave a constant value of $A = 0.09$ while in H_3PO_4 , hematite gave $A \sim 10$. The reaction rate coefficients, k , decreased in the order $H_3PO_4 > HCl > H_2SO_4$. However, the reaction orders, n , with respect to molar acid concentration were 1.5, 2.3, and 1.25 for H_3PO_4 , HCl , and H_2SO_4 , respectively, at concentrations up to 6 M. Azuma and Kametani²⁶ observed reaction orders of 1.2–1.8 for the same acids. The latter also measured the temperature dependence of the dissolution process: 18.2 to 21.9 kcal/mol. This relatively low value is approximately one-half that obtained by Gorichev et al., which suggests that the particle size used by Azuma and Kametani was large enough that diffusion through the material limited the reaction rate. This phenomenon may be expected to lead to an $(n + 1)/2$ reaction order with respect to acid concentration, rather than n . Thus, if the *intrinsic* reaction rate in HCl displays a reaction order of 2.3, the Azuma and Kametani data may be expected to yield $n = 1.65$; this is quite close to their observed value of 1.8.

Azuma and Kametani²⁶ also explored the effect of anion complexer strength. A direct relation between stability constant of the Fe^{3+} /anion complex and dissolution rate was found. Of all the acids examined, HF , which forms the most stable Fe^{3+} complex, was found to be the most vigorous solvent. Gorichev et al.¹⁸ also investigated the effect of the anion of the acid. They found that data for all of the acids at various concentrations could be represented as one plot of α vs. $t/t_{0.5}$, where $t_{0.5}$ is the half-life of the oxide. This has been interpreted to mean that the rate-determining step is the product of two independent functions and may represent the same mechanism for all of the acids.²⁷ Thus, the rate coefficient of Equation (16) may be expressed by

$$k = f(T, E, H^+), \quad (19)$$

where E is the potential for $Fe^{3+} + e^- = Fe^{2+}$ and T is the temperature. The rate of dissolution has been shown to be related to the transfer of protons from the acid to the iron oxide.²⁸ The dependence of the specific rate of dissolution, Equation (19), on the potential was shown by Gorichev et al. to translate into a dependence on the concentrations of Fe^{2+} , Fe^{3+} , and the anion of the acid. This may be expressed by

$$k = k_j (a_H^+)^{0.5} (a_{Fe}^{2+})^{0.5} (a_{Fe}^{3+})^{-0.5} (a_{An}^{y-})^u, \quad (20)$$

where a_j is the activity of species j and (a_{An}^y) is the activity of the anion. Gorichev et al. found $u = 0.5$ for SO_4^{4-} and PO_4^{3-} and $u = 0.7$ for Cl^- . Thus,

$$d\alpha/dt = k_j (a_H^+)^{0.5} (a_{An}^{y-})^u (a_{Fe}^{2+}/a_{Fe}^{3+})^{0.5} \alpha^m (1 - \alpha). \quad (21)$$

A significant conclusion of the Gorichev et al. work may be summarized as follows: additives, which shift the potential in the negative direction, accelerate the dissolution of iron oxides.

Whenever acids are actually used to remove iron oxide from steel or iron, organic corrosion inhibitors are frequently used. While accelerative and inhibitive effects on the dissolution kinetics of the oxide have been observed,^{29,30} few authors have tried to rationalize the results. Cumper et al.³¹ looked at the effect of heterocyclic nitrogen compounds (indole and pyrrole) on the dissolution rate of magnetite in 2N HCl . When

excess acid was used, the dissolution rates obeyed first-order kinetics for the first one-half of the dissolution process.

Pyrrole, indole, and 2,5-dimethylpyrrole all enhanced the dissolution rate, and pyrrole was the most powerful enhancer. The enhancement is explained by adsorption of the ring compound onto magnetite-pyrrole through its lone pair of electrons, and indole via its lone pair and its system.

Reaction Kinetics in Chelants

The work of Gorichev²⁰ on the dissolution of magnetite in Na₂EDTA closely paralleled his studies in mineral acids. The data were found to fit Equation (15) very well when $A = 0.01$. A measured activation energy of 39 kcal/mol was evidence for the lack of mass transport limitations on the rate. It should be noted that the pH dependence of the rate was found to be more complex than in the case of the acids. A maximum in the rate at 140–176°F (60–80°C) occurred at a pH (controlled by H₂SO₄) of 2.3 and at $a = 0.6$. The rate coefficient, k , was found to be independent of EDTA concentration (zero order). The rate of dissolution was found to depend both on $[H^+]$ and on the oxidation/reduction potential of the solution, just as in the case of the mineral acids. The reaction order with respect to H^+ was assumed to be 0.5, leading to a rate expression similar to Equation (21):

$$d\alpha/dt = K_J(a_H^+)^{0.5}(\gamma_{\text{RED}}/\gamma_{\text{OX}})^{0.5}(C_{\text{II}}/C_{\text{III}})^{0.5}\alpha^M(1 - \alpha), \quad (22)$$

where C_{II} and C_{III} are the overall concentrations of Fe(II) and Fe(III) containing ions, and γ_{RED} and γ_{OX} are the fractions of the free ions (i.e., Fe^{2+} and Fe^{3+}). The composition of the Fe(II) and Fe(III) complexes depends on the pH. The increase in dissolution rate brought on by increasing a_H^+ results in formation of the complex $\text{H}[\text{Fe(II)EDTA}]$. Reducing the pH to less than 2.3 causes a decrease in the dissolution rate, which is brought on by decomposition of that complex.

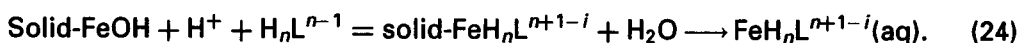
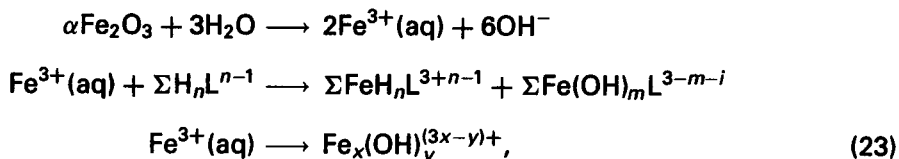
Other work on the mechanism of magnetite dissolution in chelants was recently reported. Hausler³² looked at magnetite dissolution in ammonium EDTA at pH values from 4.2 to 7.0, and found that hydrazine accelerated the dissolution rate at a pH of 7 but not at 4.2. Instead of invoking the accepted reductive dissolution mechanism, he proposed an unusual $\text{N}_2\text{H}_4\text{-Fe(III)EDTA}$ complex to explain his results.

Frenier³³ investigated magnetite dissolution from steel surfaces. He demonstrated that the protons could be supplied by ammonium ions (NH_4^+) at a pH of 9. Also, the reaction rate depended on the strength of the iron-chelating agent; the Fe(II) species presumably is stabilized. Thus, the reaction rates were found to decrease in the order $\text{EDTA} > \text{NTA} > \text{citric acid}$. Because of the importance of EDTA-type chelating agents to the practice of modern chemical cleaning of steel surfaces, this subject is considered in more detail in the next section.

Rubio and Matijevic³⁴ looked at the dissolution of FeOOH in EDTA. The maximum rate occurred at a pH of 9.7. This was interpreted to mean that dissolution of FeOOH involves adsorption of EDTA and stabilization of the ferric EDTA species. Thus, different oxidation states of iron in the scale may lead to completely different dissolution mechanisms.

A series of papers^{33–38} expanded our knowledge of the adsorptive behavior of chelating agents and the role of surface interactions in the dissolution mechanism.

These studies were directed toward understanding deposit removal from nuclear steam generators. Chang et al.³⁵ showed that the adsorption of EDTA and other polyamine polycarboxylate acid chelants onto hematite is strongly pH dependent and becomes very weak above a pH of 9.0. While the absolute amounts of chelant absorbed vary with chelant structure, they all follow the same "master" curve when normalized for molecular size. When the dissolution of hematite was investigated by Chang and Matijevic,³⁶ a very complex function of chelant structure, pH, and temperature emerged. Two mechanisms were proposed to account for the observed behavior.



The mechanism of Equation (23) dominates at a pH of 9.0, while the mechanism of Equation (24) dominates at lower pH values, where adsorption is maximized. No correlation was found between the dissolution rate and the thermodynamic properties of the closely related chelants. This observation contrasts with that of Frenier,³³ who claimed that a relationship exists between dissolution rate and thermodynamic properties at a pH of 9.2, when ammoniated chelants are used to remove iron oxide from steel surfaces.

The dissolution of magnetite in EDTA was described by Blesa and Maroto,³⁹ whose pH vs. reaction rate data were significantly different from those obtained by Chang and Matijevic³⁶ for hematite. Both authors found decreased dissolution at a very low pH (4.5) compared with moderate pH values (6); however, Blesa and Maroto found even lower rates at a pH of 8, while Chang and Matijevic found just the opposite effect. Their studies were conducted at 77°F (25°C). As the temperature was raised, the chelants in both cases became much more effective at lower rather than at high pH values. Blesa and Maroto³⁹ claimed that the adsorbed EDTA blocks the surface and thus retards dissolution. As the temperature is raised, this blocking action presumably becomes less effective, and the rate of oxide bond scission exceeds that of chelant/oxide formation.

As mentioned earlier, many iron oxide dissolution curves have a pronounced induction period that is characteristic of an autocatalytic process. In describing the dissolution of magnetite by oxalic acid, Baumgartner et al.⁴⁰ proposed a mechanism in which the ferrous oxalate ion catalyzes the dissolution through a fast electron transfer reaction (reductive dissolution). They proved this thesis by adding more ferrous ions and noting the disappearance of the induction period. An important insight is that chelated ferrous ions can act as reducing agents for ferric ions in the scale if the chelant preferentially stabilizes the oxidized state with respect to the reduced state. Presumably, this is true for oxalic acid. It definitely is true for EDTA and citric acid at a pH of ~9.⁴¹ Recent work showed that the standard cell emf (E_0) is changed by 790 mV (in the negative direction) for iron EDTA and 990 mV for iron citrate as compared with the aquo couple. Thus, the mechanism proposed by Baumgartner et al. is probably active in other chelant systems.

In the absence of a steel surface, reducing agents are frequently added to chelant solvents to increase the reaction rate of magnetite dissolution. Mixtures of ammonium EDTA and N_2H_4 were developed to remove deposits from nuclear steam generators. A great deal of work was done to develop practical solvents for cleaning the secondary side of steam generators, but the five references listed⁴²⁻⁴⁶ are illustrative of the process. These authors apparently assume that N_2H_4 fosters the reductive dissolution mechanism, but the details are not addressed. The one exception is Hausler,³² who favors an unusual iron hydrazine complex. Because the deposits in nuclear steam generators frequently contain mixed oxides, such as iron/chromium and iron/nickel species, other reducing metal complexes were suggested. These are called low oxidation state metal ion (LOMI) reagents and include Fe(II)EDTA, Cr(III), and V(II) picolinate. These materials have been used extensively to clean the primary side (usually called decontamination). Presumably, they catalyze scale dissolution by the Baumgartner mechanism. More details of nuclear deposit removal is described in Chapter 7.

Morphology of Oxides

Experience in the chemical cleaning industry has shown that no two iron oxides are alike. The heat history, density, and impurities may have a very large effect on the actual rate of deposit removal. Azuma and Kametani^{26,47} made systematic studies of the effect of sample preparation on oxide dissolution. The formation temperature of the oxide markedly influenced the dissolution rate. The physical properties apparently controlling the reaction were the surface area (calculated by a permeability method) and a normalizing factor that is dependent on the aggregate crystal structure. Baud and Ferrier⁴⁸ and Fields⁴⁹ also demonstrated the importance of the scale structure (layers and microcracks). McPherson⁵⁰ showed that the presence of chromium-containing spinels has a marked influence on deposits found in the superheat or reheat sections of power boilers.

Dissolution of Free Magnetite

Recent work on the dissolution of powdered magnetite led to an increased understanding of environmental factors affecting its rate of dissolution in aqueous media. A significant conclusion of the Gorichev et al. work¹⁶⁻²⁰ is that additives, which shift the solution potential in the negative direction, accelerate the dissolution of magnetite. In mineral acid, formation of Fe^{2+} increases the rate, while Fe^{3+} decreases it. In aqueous Na_2EDTA , conditions that favor formation of $HFe(II)EDTA$ accelerate the dissolution. The reaction order with respect to $[H^+]$ is 0.5 in the mineral acids; in chelants, however, the pH dependence of the rate is not simple. In chelants, complexes that can involve H^+ and thereby affect the dissolution rate are formed. Furthermore, in Na_2EDTA , the rate appears to be independent of $[Na_2EDTA]$.

The adsorption effect of chelating agents onto the oxide appears to be very complex and probably is controlled by the pH, ZCP of the oxide, and the temperature. The action of the LOMI reagent (including ferrous ions) helps to explain the S shape and complex kinetics of many dissolution curves.

In the absence of an applied potential, the dissolution of free magnetite in mineral acids proceeds according to the following proposed mechanism (mass and charge balances are not attempted).¹⁶

- (a) $\text{Fe}_3\text{O}_4 + 2\text{H}^+ \longrightarrow \text{Fe}_2\text{O}_3 + \text{Fe}^{2+} + \text{H}_2\text{O}$,
- (b) $\text{Fe}_3\text{O}_4 + \text{H}^+ \longrightarrow \text{FeO}_x + \text{Fe}^{2+} + \text{H}_2\text{O}$,
- (c) $\text{FeO}_x + \text{Fe}^{2+} + \text{An}^{Y-} \longrightarrow (\text{FeO}_{x-1})_Y \text{An}$,
- (d) $(\text{FeO}_{x-1})_Y \text{An} \longrightarrow (\text{FeO}_{x-1})^{(x-1)+} + \text{An}^{Y-}$,
- (e) $(\text{FeO}_{x-1})^{(x-1)+} + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{H}_2\text{O}$.

Current data suggest that (c) is the slowest step of the reaction. Development of the surface area of the FeOx phase during the early stages of dissolution might be manifested in the form of an induction (incubation) period. Experimental evidence confirms the presence of an induction period. Consistent with this picture are the good fits of the data in all media (acids with or without chelants) to Equation (15). However, the above mechanism does not properly account for the lack of an induction period in the case of Fe_2O_3 dissolution; that is, dissolution of either Fe_3O_4 or Fe_2O_3 should, according to the mechanism, lead to formation of FeOx, whose decomposition is presumed to be the slow step. This criticism could be eliminated, however, if the initial disproportionation reaction, step (a), is even slower than step (c). This is indeed a strong possibility because step (a) involves two rather slow processes—lattice restructuring and solid-state diffusion of O^{2-} .

Equation (15) contains only information about the development of an active surface area. It contains no information about the dissolution medium. For mineral acids¹⁸ and Na_2EDTA ,²⁰ Gorichev et al. developed Expressions (20) and (21), respectively, which contain explicit information about the dependence of the rate on the activities of H^+ , An^{Y-} , free Fe^{2+} and Fe^{3+} , and chelated Fe^{2+} and Fe^{3+} . The observed reaction order, n , with respect to acid concentration is significantly greater than that given by Equation (21) or Equation (22). The different reaction orders may be reconciled by considering that at a high concentration, the activity of a solute does not linearly vary with molar concentration. For example, increasing the molar concentration of HCl from 1 to 4 M increases the activities of H^+ and Cl^- by a factor of 8, rather than 4. Hence, Equation (21) may be expressed by

$$d\alpha/dt = k_f[\text{H}^+]^{1.0}[\text{Cl}^-]^{1.4} \{[\text{Fe}^{2+}]/[\text{Fe}^{3+}]\}^{0.5} \alpha^m (1 - \alpha) \quad (25)$$

in the concentration range of 1.0 to 4.0 M. (Actually, this expression would be satisfactory down to 0.05 M.) The sum of the reaction orders for H^+ and Cl^- is 2.4, which is quite close to the observed value of 2.3.¹⁸

Equations (2) and (25) are difficult to work with because values of $a\text{Fe}^{2+}/a\text{Fe}^{3+}$ or $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ are required. These are generally not measured. Hence, further development of kinetics treatments, with an eye toward eliminating the dependence of the rate on $a\text{Fe}^{2+}/a\text{Fe}^{3+}$, appears to be in order. Parametric studies may reveal an appropriate correlation of $a\text{Fe}^{2+}/a\text{Fe}^{3+}$ with commonly measured properties. Also, the surface area development term in Equations (16), (21), and (24), that is, $\alpha^m(1 - \alpha)$, must be rewritten in more fundamental terms so that *bulk* magnetite as well as powdered magnetite may be adequately described by these relations. The porosity and cylindrical pore models of Simons^{51,52} and Petersen,⁵³ respectively, may serve this purpose.

Dissolution of Iron Oxide from Steel Surfaces

Compared with the large amount of work on the mechanism of free iron oxide dissolution, there is relatively little information available on the dissolution of oxides from steel surfaces.^{9–11,32} A major contribution of these studies is confirmation that the reductive dissolution mechanism is operative, thus leading to oxidation of the base metal at the expense of ferric reduction in the scale. Because operational iron oxide scales undoubtedly contain numerous microcracks,⁴⁹ the anodic reactions probably take place at these cracks.

Figure 1 is a schematic representation of the author's thinking on magnetite dissolution from a ferrous metal surface. The iron is oxidized at the microcracks, releasing electrons that reduce Fe^{3+} in the scale. The Fe^{2+} ions can pass across the Helmholtz layer into the bulk solution. Protons also cross the double layer to react with the oxide ions initially forming OH^- ions. The passage of the products across the interphase is considered the rate-determining step. Properties of the solution that are known to influence the reaction rate include the presence of strong complexers such as chelants (EDTA) and inorganic reactants, for example, F^- ions, and the pH. The complexers affect the rate by removing Fe^{2+} ions from the region around the double layer or by changing the surface charge, thereby changing the potential.¹ While the rate may depend on the strength of the complexer,^{12,13,26,29,33} it may not depend on the concentration of a free complexer.¹⁷ However, the pH has a marked effect on the rate. Most authors suggest a half-order dependence on $[\text{H}^+]$ in the absence of complexing agents, but the pH dependence in complexer solutions is far from straightforward.²⁰

Two overall equations can be written for magnetite dissolution from steel surfaces. Equation (26) summarizes the species that are involved when no chelant is present:

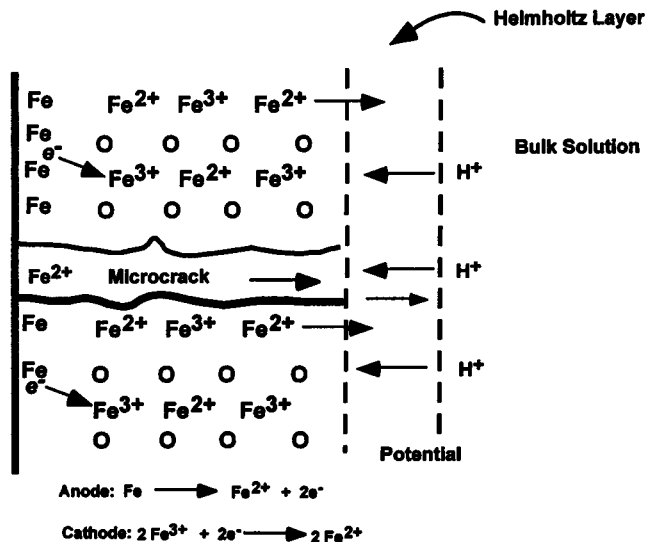
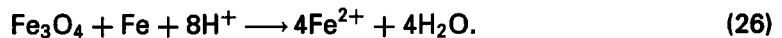


Figure 1. Iron oxide dissolution mechanism.

If a chelant is present, Equation (26) becomes



While the more general aspects of the mechanism seem to be worked out, many details of the kinetics still have to be established. The dissolution of bulk Fe_3O_4 on steel must be examined by means of detailed studies such as those of Gorichev et al.; these will, out of necessity, entail flow experiments, for example, in a loop or with rotating disk specimens. Electrochemical studies of such composites also would be of use. A major problem will continue to cloud experiments in which the concentration of Fe in solution is used as the primary kinetic marker; the corrosion of the base metal by the solution (with or without inhibitors) must be subtracted from the oxide dissolution rate. Unfortunately, no information exists on the effect of the oxide cover (other than passive layers) on the corrosion rate of the base metal. Finally, the scale morphology may play a major role in the application of these theories to the descaling of real heat transfer equipment. The author notes that much of this review is taken from an article by Frenier and Growcock.⁵⁴

DETAILS OF MAGNETITE REMOVAL FROM STEEL SURFACES IN CHELANT SOLUTIONS

Because chelating agents are such important materials for removing fouling deposits and surface films from industrial equipment,⁵⁵⁻⁶¹ additional details of the removal mechanisms from steel surfaces have been worked out. The mechanism of removal varies according to the chemical and physical environment of the metal to be chelated. Because of this complexity, this discussion is restricted to the removal of magnetite (Fe_3O_4) from steel surfaces.

Suggestions for a general deposit removal mechanism and a description of the research supporting the several reaction steps are presented. Chelants are used from a pH of 3.0 to 9.5; however, most of the examples are from the alkaline range because the unique factors are accentuated under these conditions.

This investigation considered four factors that are thought to control the rate of the scale dissolution reaction: (1) reduction of Fe^{3+} ions in the scale; (2) type of cation; (3) chelating agent structure; and (4) temperature.

Reductive Dissolution Tests

Magnetite was produced by heating mild steel in steam at 1112°F (600°C). The coupons were bent, and sheets of magnetite were popped off. A sample of scale of $\sim 5 \text{ cm}^2$ surface area was digested in 150 mL of 0.13 M $(\text{NH}_4)_4\text{EDTA}$ (pH of 9.2) at 203°F (95°C). In a companion test, another sample was electrically connected to a steel coupon and similarly digested. Rates of dissolution were computed from weight loss and determination of iron in solution by using the orthophenanthroline method.

Reductive dissolution was also studied by determining the oxidation state (2+ or 3+) of the iron during simulated, dynamic scale dissolution tests. The ratio of $\text{Fe(II)EDTA}^{2-}/\text{Fe(III)EDTA}^-$ can be determined by measuring the redox potential (emf) of the solution. For a one electron change at 77°F (25°C), the Nernst equation

predicts that

$$E = E_0 - 0.059 \log[\text{Fe(II)EDTA}^{2-}]/[\text{Fe(III)EDTA}^-], \tag{28}$$

assuming concentration equals activity. Here, E is the redox potential of the cell and E_0 is the standard redox potential at unit activity. Thus, a plot of emf vs. $\log[\text{Fe(II)EDTA}/\text{Fe(III)EDTA}]$ should give a straight line with a slope of -0.059 mV. For the iron/EDTA system, this was measured (with the cell described in Reference 41) by following emf changes during the air oxidation of $[\text{Fe(II)EDTA}^{2-}]$. Note that Fe(II)EDTA^{2-} is colorless in the visible spectrum, but at a pH of 9.2, Fe(III)EDTA^- has a strong absorbance at 345 nm as measured on a Beckman DB spectrophotometer. From a Beer's law plot of absorbance vs. concentration, $[\text{Fe(III)EDTA}^-]$ could be determined and $[\text{Fe(II)EDTA}^{2-}]$ calculated from knowledge of total Fe in solution.

A stock solution of Fe(II)EDTA^{2-} was prepared by refluxing iron powder with 10% tetra-ammonium EDTA for 36 h, followed by filtration to remove unreacted iron. The solution was reduced to Fe(II)EDTA^{2-} by stirring with excess 64% N_2H_4 overnight. The total Fe concentration was then determined by atomic absorption. For the emf relationships to be determined, 750 mL of 4% tetra-ammonium EDTA was thermostated at a desired temperature, and prepurified N_2 was bubbled through for 1.5 h. Enough stock Fe(II)EDTA^{2-} was introduced to give a desired total Fe concentration (usually 0.8%), and the pH was carefully adjusted by passing NH_3 through the solution, or by adding glacial acetic acid. The potential (emf) of the solution was measured between a saturated calomel electrode (SCE) and the platinum electrode with an NLS X-2 digital voltmeter. Air was introduced with a gas sparge; at various intervals, the emf was recorded and the $\text{Fe(II)EDTA}^{2-}/\text{Fe(III)EDTA}$ ratio was spectrophotometrically determined on aliquots. At all times, the pH was maintained at a ± 0.05 pH unit. By the use of various pH values, plots of emf vs. $[\text{Fe(II)}]/[\text{Fe(III)}]$ were developed. As a check, runs were made by adding known amounts of ferrous and ferric sulfate to ammonium EDTA. These points fell on the same line as those determined with Fe(II)EDTA^{2-} made from digested Fe. Therefore, if the pH and temperature are known, the ionic ratio can be determined from the emf solution. Note that the slopes are somewhat different from those predicted by the Nernst equation, and there is a strong pH dependence. A dynamic test loop was used to simulate cleaning environments. The loop was a completely PTFE-coated circulation system capable of maintaining temperatures above 320°F (160°C) and pressures above 725 kPa. The volume was ~34 L, and flow could be regulated from 0 to 270 L/min.

For the purpose of this test, a 3-ft (91-cm) section of 6.35-cm ID boiler tubing taken from a Midwestern U.S. drum boiler was used. An x-ray diffraction analysis of the scale is seen in Table 1.

TABLE 1
Analysis of Scale Used in the Loop Test

Material	Percent
Fe ₃ O ₄	35–45
Fe ₂ O ₃	30–40
Cu	15–20
Cu ₂ O	5–10

The loop was filled with 6% tetra-ammonium EDTA at a pH of 9.2, purged with N₂ for approximately 1 h, and brought to an operating temperature of 320°F (160°C) with a flow velocity of ~300 cm/s. During the first hour, samples were taken every 10 to 15 min, and [Fe] was determined by atomic absorption (AA) spectrophotometry. After the first hour, samples were taken every 30 min. The emf was determined by running a sample into a 100-mL cell containing a Pt and a saturated calomel electrode. Prior to taking the sample, the cell was purged with N₂ for 5 min. From the emf solution and the [Fe], ionic concentrations were calculated. Details of these data are found in Reference 33.

Autoclave Cleaning Tests

A number of high temperature, magnetite dissolution tests were run in 1-L titanium autoclaves. Transfer flasks were fabricated from AISI 316 stainless steel so that a concentrated chelant solution could be injected into the autoclave when the test temperature had been reached.

All of the kinetic tests were conducted by using the same batch of tubing obtained from an operational northeastern U.S. drum boiler. The tubes were machined to a constant OD (3.34 cm) and length (4.74 cm) with a total surface area of 102.8 cm². The interior surfaces were coated with about 1 g of oxide and 50 mg of Cu. The composition of the scale as determined by x-ray diffraction and the chemical composition of the boiler tube are shown in Table 2. In each of the dissolution tests, two AISI 1010 carbon steel coupons in a PTFE mount were added to give a total wetted surface area of 190 cm². The chelating agents tested were obtained from commercial sources and were used without further purification. The chelants and their iron formation constants are described in Table 3.

To conduct the scale dissolution test, the tube sample, 0.10% commercial corrosion inhibitor, corrosion coupons, and 250 mL of H₂O were put into a glass liner and then into the autoclave. The vessel was heated to the test temperature, usually 320°F (160°C), and stirred at 200 rpm.

A total of 50 mL of the concentrate chelant solution was drawn into an evacuated transfer bomb, which then was pressurized with N₂ to about 725 kPa. At the starting

TABLE 2

Analysis of Tube and Scale Used in the Autoclave Tests

Wt. % Concentration of the Tube Metal							
Fe	Mn	Mo	Cr	Si	C	S	P
98.8	0.59	0.016	0.044	0.18	0.06	0.04	0.01

Scale Analysis:

X-ray Diffraction and Fluorescence

Fe ₂ O ₃	major
Fe ₃ O ₄	<15%
Cu	trace
Ni	trace

TABLE 3

Chelants and Formation Constants

Ligand	log K for 1:1 Complex ⁶²	
	Fe(II)	Fe(III)
Citric acid	4.4	11.5
NTA	8.3	15.9
HEDTA	12.2	19.8
EDTA	14.2	25
DTPA	16.5	28

time, the chelant was blown into the reactor by using a high-pressure nylon hose. The chelant concentration was 0.12 M. At intervals, 1–2 mL of solution was withdrawn after the sample line was blown down with N₂. The samples were analyzed for [Fe] by atomic absorption spectroscopy. At the end of the test (4–6 h), the samples were removed. The tube was rinsed with acetone and examined under low-power magnification for the presence of scale. The tests were run in duplicate. Details are given in Reference 54.

Reductive Dissolution

The reductive dissolution of magnetite is well established in acidic solutions.^{63,64} According to this mechanism, Fe₃O₄ dissolves and directly releases Fe²⁺ ions, and the base metal or some other reducing agent is consumed. This mechanism may also be active in chelate solutions. Magnetite electrically coupled to steel coupon dissolves at a faster rate than isolated scale (Table 4). Pocock and Leedy⁴³ compared a number of solvents for the removal of Fe₃O₄ from nuclear steam generators. Because the generators contained little carbon steel, chemical reducing agents were used. A solution of hydrazine and ammonium EDTA was the most effective solvent. In these tests, Fe₃O₄ was stirred into an autoclave with ammonium EDTA at a pH of 7.5 and a temperature of 203°F (95°C). The chemical reducing agent accelerated the dissolution rate (Table 5).

The ionic concentrations during the 6 h of the dynamic cleaning of the tubing described in the experimental section (Table 1) are shown in Figure 2. It is clear that there is appreciable Fe³⁺ present only during the first 2 h of cleaning, and the Fe²⁺ species quickly becomes the dominant ion.

The data from these three experiments indicate that reductive dissolution occurs in ammonium EDTA solutions. Although some magnetite may directly dissolve, releasing ferric ions that subsequently reduce on the bare steel, reduction of ferric iron in the scale by base metal or N₂H₄ appears to predominate. The accelerative effect of reductive dissolution in acidic solution^{62–64} is frequently attributed to potential changes

TABLE 4

Reductive Dissolution Test, 0.13 M (NH₄)₂EDTA, 203°F (95°C)

Scale Condition	Rate (g/cm ² /h)
Isolated	1.3 × 10 ⁻²
Electrically coupled	7.1 × 10 ⁻²

TABLE 5

Hydrazine Concentration Test, (NH₄)₂EDTA,
pH of 7.5, 203°F (95°C)^(A)

% N ₂ H ₄	% Fe ₃ O ₄ Dissolved			
	2 h	4 h	6 h	8 h
0.25	21	25	28	26
1.0	67	84	86	90

^(A)Reproduced with permission from F. Pocock and W. Leedy.⁴³

across the Helmholtz layer. Hickling and Ives⁶⁵ invoked an electron-jump mechanism that confers mobility on the Fe²⁺ ions. Because potentials of the magnetite could not be measured at cleaning temperatures in ammonium EDTA, the detailed mechanism is more speculative in the chelant systems.

Magnetite Dissolution Tests in Pressure Bombs

The Erofeev empirical equation,⁶⁶

$$-\ln(1 - \alpha) = kt^n, \quad (17)$$

was used to treat the iron dissolution data. In most cases, the boiler tubes were 100% clean after 6 h, and the fraction dissolved (α) was calculated from the final concentration of Fe in solution at the end of the tests. In those cases in which the tubes were not clean, a final [Fe] of 3000 ppm, based on the average data from the other tests, was used to estimate α . The reaction order, n , and the dissolution rate constant, k , were calculated from a log-log plot of $\ln(1/1 - \alpha)$ vs. t .

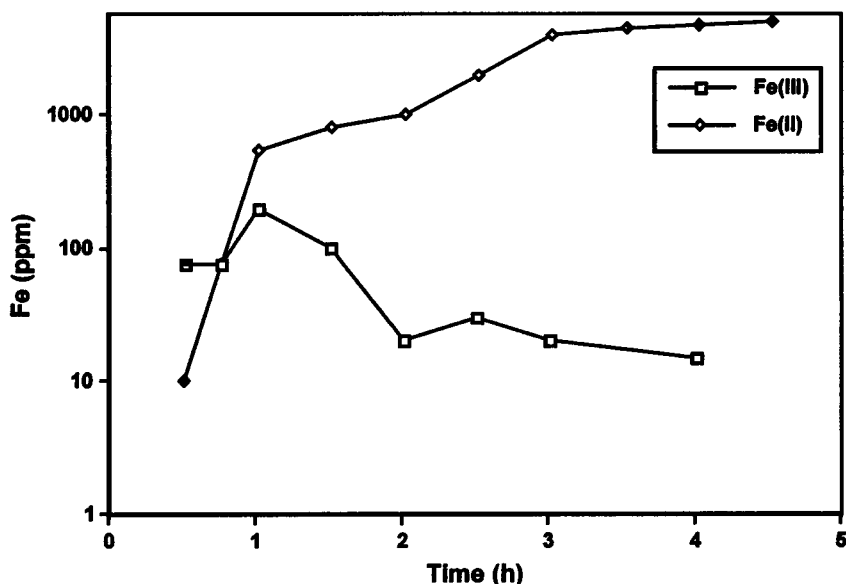


Figure 2. Concentrations of Fe(II) and Fe(III) during tube cleaning at 320°F (160°C).

TABLE 6

Rate Constants for Iron Oxide Dissolution in Ammonium Chelant Solutions

Iron Oxide Dissolution at a pH of 9.2; Adjusted with NH ₄ OH, 0.12 M Chelant, 320°F (160°C)			
Chelant	<i>k</i> (h ⁻¹)	<i>n</i>	Rate, 1018 (lb/ft ² /day) ^(A)
Citric acid	0.08	0.65	0.005
NTA	0.12	0.20	0.004
EDTA	0.28	0.70	0.005
HEDTA	0.28	0.96	0.003
DTPA	0.35	0.65	0.004

^(A)5 Kg/m²/day.

The rate constants and corrosion rates of the 1010 (carbon steel) coupons for five ammonium chelants tested at 320°F (160°C) are shown in Table 6. The dissolution curves are seen in Figure 3. The EDTA was tested with two different cations – Na⁺ and NH₄⁺. The cation effect is shown in Table 7 and Figure 4. The effect of temperature is described in Figure 5 and Table 8. The corrosion rates of the 1010 CS coupons were very low, indicating that the iron detected was associated mostly with scale dissolution, not general solvent corrosion.

Gorichev²⁰ reported substantial kinetic data for the dissolution of free magnetite in sodium EDTA. The kinetic curves showed a characteristic S shape and are similar to Figures 3, 4, and 5. They reported a zero-order dependence on [EDTA] and an 0.5-order dependence on [H⁺], and they stated that the driving force is the potential jump at the oxide/electrolyte interface, which is determined by the difference in the stability constants of the Fe²⁺ and Fe³⁺ species. In a series of tests of electrically coupled

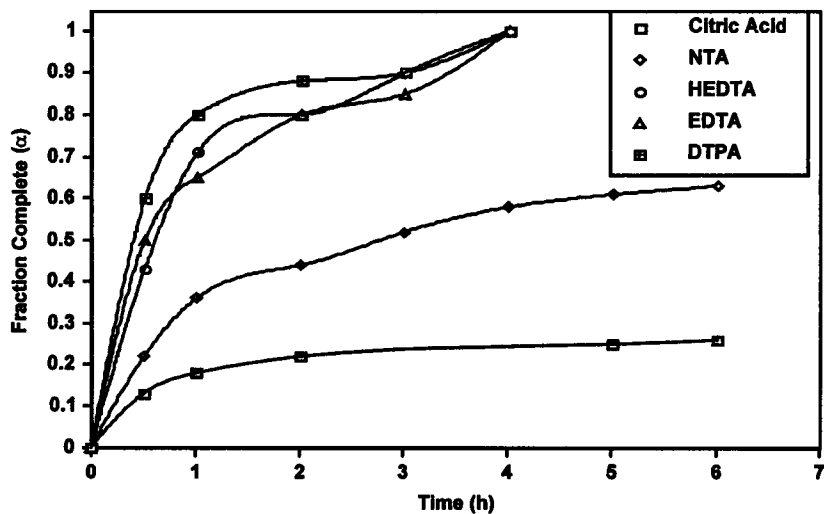


Figure 3. Iron oxide dissolution tests in ammonium chelates at a pH of 9.2; tests were run at 320°F (160°C).

TABLE 7

Rate Constants for Iron Oxide Dissolution in Na⁺
and NH₄⁺ EDTA

Iron Oxide Dissolution at a pH of 9.2 with 0.12 M EDTA, 320°F (160°C)			
Buffer	k (h ⁻¹)	n	Rate, 1018 (lb/ft ² /day) ^(A)
NaBO ₃	0.003	—	0.002
NH ₄ OH	0.28	0.70	0.005

^(A) 5 Kg/m²/day.

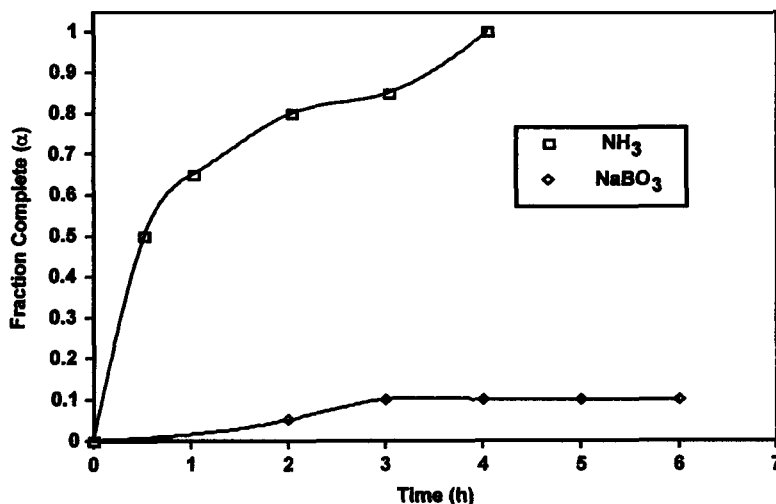


Figure 4. Iron oxide dissolution tests at a pH of 9.2 with EDTA test temperature at 320°F (160°C).

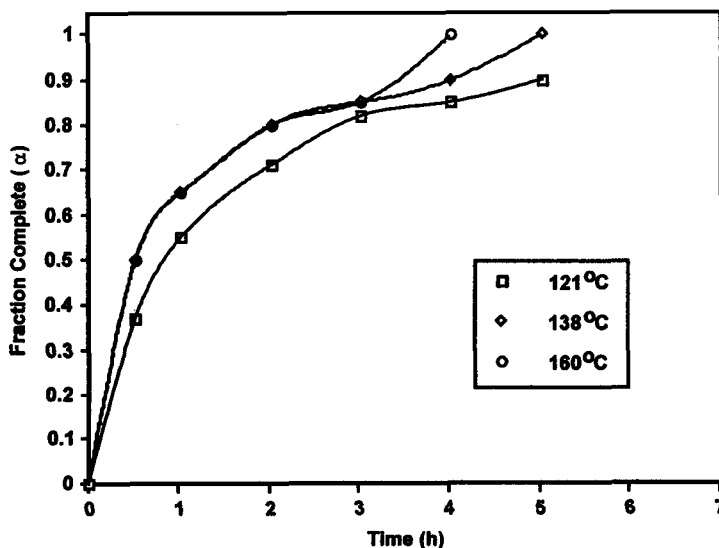


Figure 5. Iron oxide removal tests in ammonium EDTA at a pH of 9.2.

TABLE 8

Rate Constants for Iron Oxide Dissolution
Temperature Effects in (NH₄)₄EDTA

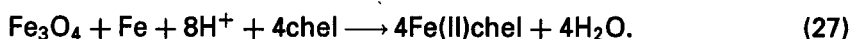
Iron Oxide Dissolution at a pH of 9.2, 0.12 M (NH ₄) ₄ EDTA			
Temp, °C	<i>k</i> (h ⁻¹)	<i>n</i>	Rate, 1018 (lb/ft ² /day) ^(A)
160	0.28	0.70	0.005
130	0.28	0.63	0.005
120	0.12	0.72	0.003

^(A)5 kg/m²/day.

magnetite, Brunet¹⁶ found that the reaction order with respect to EDTA ranged from 0.36 to 0.63.

In the present case, in which the magnetite is also electrically coupled to steel and reductive dissolution is invoked, a more conventional mass action mechanism can be proposed wherein the chelant removes Fe²⁺ (and some Fe³⁺) ions from the interface. The rate coefficients (*k*, Table 6) are in the same order as the Fe²⁺ stability constants (Table 3) of the ligands tested (citric < NTA < HEDTA = EDTA < DTPA), but the differences in the rates are large only when the weak chelants are compared with the strong ones. At a pH of 9.2, citric acid is such a poor complexer for Fe²⁺ that the reaction rate is almost zero. This observation of the effect of complexer strength is similar to that of Azuma and Kametani,²⁶ who reported that mineral acids with strong complexing ions (e.g., HF) were more active solvents than those (H₂SO₄) with weaker complexers. A total reaction order of <1.0 was observed in all of the tests. Fractional reaction orders indicate complex mechanisms and are observed when the rate-controlling step is limited by diffusion. This total reaction order is in the same range as that reported by Burnet.¹¹

When sodium is substituted for ammonium in the chelant formulation, the reaction rate becomes very low at alkaline pH values. Both Gorichev⁶⁷ and Lesinski⁵⁵ made similar observations. Apparently the ammonium ion provides the protons necessary to support the scale dissolution reaction.



Because ammonia is at its maximum buffer point (pH of 9.2), the pH remains almost constant. The results described in Table 7 and Figure 4 were designed to confirm the effect of the proton donor on the scale dissolution reaction. The NaBO₃ was chosen as the basic component instead of NaOH so that a buffer comparable to NH₄OH would be present. Thus, large pH changes should not have obscured the cation effect.

The effect of temperature change on the rate of magnetic dissolution in (NH₄)₄EDTA is shown in Figure 5 and Table 8. While the data are insufficient to calculate an activation energy with precision, the temperature dependence is definitely small (~15 kcal/mol) in the range tested. This small number suggests a diffusion limited, rate-controlling step.

From the data gathered in these experiments, the following mechanism is proposed for the dissolution of magnetite from a steel surface using an alkaline chelate (see Figure 1).

- (a) $\text{Fe} \longrightarrow 2\text{e}^- + \text{Fe}^{2+}$ anode (microcracks in scale),
- (b) $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$ cathode,
- (c) $\text{Fe}^{2+} (\text{solid}) \longrightarrow \text{Fe}^{2+} (\text{soln})$ RDS,
- (d) $\text{Fe}^{2+} + \text{chel} = \text{Fe(II)chel}$,
- (e) $\text{H}^+ + \text{O}^{2-} \longrightarrow \text{OH}^-$
- (f) $\text{OH}^- (\text{solid}) \longrightarrow \text{OH}^- (\text{soln})$.

The overall reaction is



In ammonia containing solutions, Equation (27) becomes



All relevant information indicates that step 3 (diffusion of Fe^{2+} across the Helmholtz layer) is rate determining when magnetite is in physical contact with iron or another electron source. This conclusion is most strongly supported by the small heat of activation, the fractional reaction order, and the relatively mild effect of chelating agent strength on the rate. A significant effect is noted only when very weak chelants (citrate and NTA) are used.

COPPER DISSOLUTION MECHANISMS IN CHELATING AGENTS

During copper-removal procedures that are conducted with the iron solutions of EDTA^{55,56} or citric acid^{57,58} as the reaction medium, many operators have noted that it is much easier to remove copper from plated steel in EDTA than in ammonium citrate. The observation has been difficult to explain since the procedures are about the same: the iron solutions that remain in the boiler being cleaned are oxidized with air or air + NaNO_2 . These chemicals are passed through the ammoniacal chelate solution in both cases. In an attempt to understand the mechanisms of copper removal in chelate solutions, the dissolution mechanisms in chelating agents was studied in the presence and absence of iron.⁴¹ Two types of tests (described in detail in Reference 41) were conducted.

1. Copper-plated steel coupons were cleaned in the electrochemical cell seen as Figure 6. All of the test solutions were maintained at 150°F, and various oxidizers were added to the solutions of ammonium EDTA or ammonium citrate (pH 9.5), with or without 7000-ppm ferrous Fe(II) iron.
2. Iron and copper chelate solutions were analyzed by using DC polarography (dropping Hg electrodes), using the classical methods of Kohlthoff.⁶⁸

Figure 7 shows the copper concentrations found during dissolution tests with four different Fe(II) solutions: EDTA with air; EDTA with air + NaNO_2 ; citrate + air; and citrate with air + NaNO_2 . The EDTA solutions removed $>10\times$ as much copper as the comparable citrate solutions. The EDTA solutions with the additional oxidant (nitrite) remove more copper than the air-only solution.

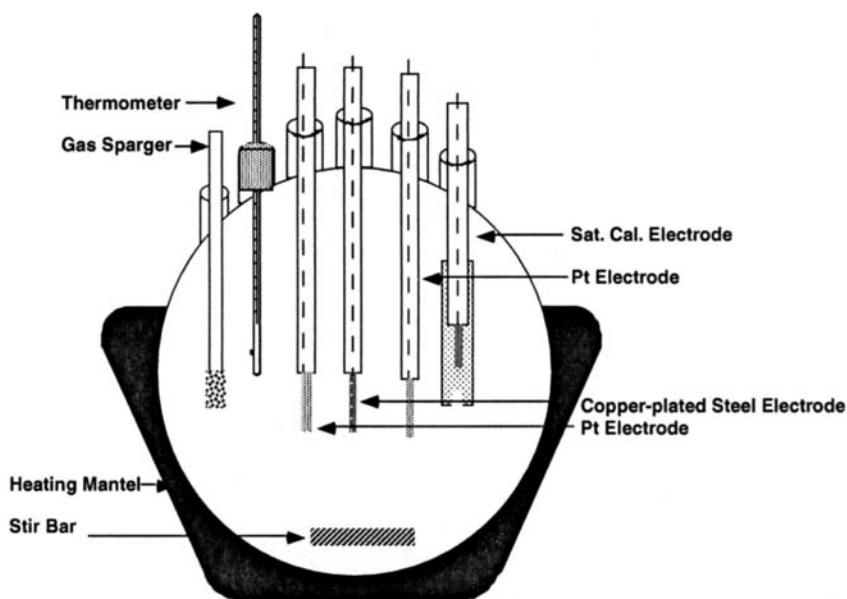


Figure 6. Copper-removal cell.

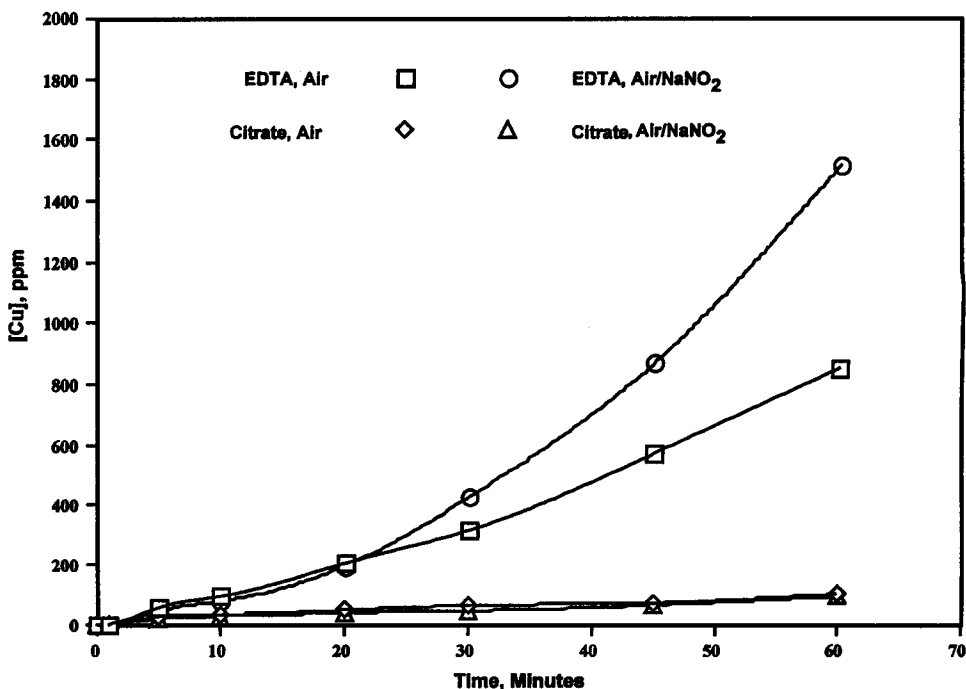


Figure 7. Dissolution of copper from plated steel in Fe(II) chelate, 7000 ppm Fe, 150°F.

TABLE 9

Polarographic Data for 0.001-m Metal Chelate Solutions

Metal	Chelate	$E_{1/2}$, meas (mV)	$E_{1/2}$, lit ⁶⁹ (mV)	I_d (mA)	Reaction
Fe(II)	EDTA	-240	-250	4.0	Fe(II) → Fe(III)
Fe(III)	EDTA	-260	-250	3.2	Fe(III) → Fe(II)
Fe(II)	Citrate	-220	-475	1.0	Fe(II) → Fe(III)
		-465		1.0	Fe(II) → Fe(III)
Fe(III)	Citrate	-475	-475	2.0	Fe(III) → Fe(II)
Cu(II)	Citrate	-179	-170	2.0	C(II) → Cu(I)
		-340	-340	2.2	Cu(I) → Cu ⁰
Cu(II)	EDTA	-475	Not known	5.0	Cu(II) → Cu ⁰

In other tests (refer to Reference 41), citrate solutions actually removed more copper in the absence of iron than in the presence of iron, while EDTA-iron solutions oxidized with H₂O₂ removed more than twice as much iron as the air-oxidized solutions.

The iron and copper chelate solutions exhibited classical oxidation and reduction waves that allowed the equilibrium (half-wave) potentials to be estimated (see Table 9).

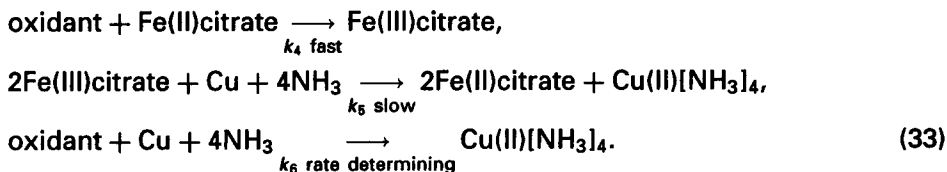
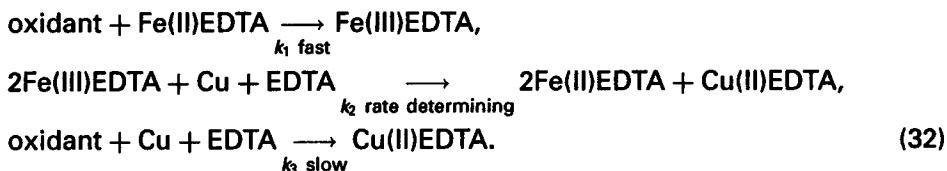
According to Kohlthoff⁶⁸, the half-wave potentials are approximately equal to the equilibrium potentials (E^0) for the reaction: oxidized species + e⁻ = reduced species. By comparing the measured half-wave potentials of the chelated species with the E^0 value for Fe²⁺ → Fe³⁺ + e⁻ (-525 mV), we can estimate the relative ratios of the equilibrium constants for the ferrous and ferric chelates of citric acid and EDTA.

$$E_{1/2}(\text{complexed}) - E_{1/2}(\text{standard}) = 0.059 \log K_{ox}/K_{rd}. \quad (31)$$

Here K_{ox} and K_{rd} are the disassociation constant for the oxidized and reduced complexes, respectively. With the use of a E^0 value of 0.525 mV for Fe(II) → Fe(III), the ratios of the equilibrium constants for EDTA are calculated to be 1.5×10^{-14} for Fe(III)/Fe(II), and 6.1×10^{-17} for the citrate couple. This calculation shows that the citrate ion stabilizes the ferric species more than 10³ times more than the EDTA ferric/ferrous couple.

The half-wave potentials for the copper citrate solutions are essentially identical to the literature values for the aquo-ammonium/copper species in solution, while the values for EDTA/Cu indicate a much more stable complex.

Based on these data, the following mechanisms are proposed.



The major oxidizing agent for the EDTA system is Fe(III)EDTA, while the external oxidizer (oxygen, nitrite) oxidizes the copper in the iron citrate system. The external oxidizer does oxidize the ferrous citrate to ferric citrate, but this species does not dissolve much of the copper; it actually acts as a sink for the external oxidizer. The only benefit of using the iron citrate solution is that an additional oxidizing fill of the unit is avoided.

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4

CORROSION, PASSIVATION, AND INHIBITION

Essentially all of the solvents used for dissolving inorganic deposits, as well as some of the solvents for organic deposits, are corrosive to some metals of construction. In addition, it may be necessary to passivate equipment after most chemical treatments to reduce additional corrosion from the atmosphere or to facilitate special processes such as some copper removal techniques. While the definitions can become blurred, passivation is thought to involve the formation of a very thin oxide coating; most of the inhibitors used in cleaning formulations contain complex organic molecules that adsorb/react at the metal surface and form barrier films. Passivation is particularly important during chelant cleaning to remove iron and copper deposits.¹⁻⁷ Both types of anticorrosion treatments will be reviewed in this chapter.

CHEMICAL CLEANING PASSIVATION TREATMENTS

Uhlig⁸ gave two definitions of passivation that are germane: (1) a metal active in the emf series (or an alloy composed of such metals) is considered to be passive when its electrochemical behavior approaches that of an appreciably less active or noble metal; and (2) a metal or alloy is passive if it substantially resists corrosion in environments in which, thermodynamically, there is a large free-energy decrease associated with its passage from the metallic state to the appropriate corrosion products. The passivating film is thought to be composed of some type of iron oxide if iron is the active metal. The formation, composition, and breakdown of passivation is a very complex subject. At a symposium sponsored by the Electrochemical Society⁹ in 1986, 21 papers were devoted to passivation theory and passivation breakdown. The formation of a passive film on carbon steel usually requires pH values of >8.5 and oxidizing conditions. Usually oxygen (or something that yields oxygen) must be present. The chemical composition of the passive film will vary depending on the aqueous fluids present, but it consists of various mixtures of iron oxides (magnetite, γ -Fe₂O₃, γ -FeOOH) or an amorphous oxide of iron. The thickness may range from about 10 to about 30 Å. While the passive film is thought to mostly consist of

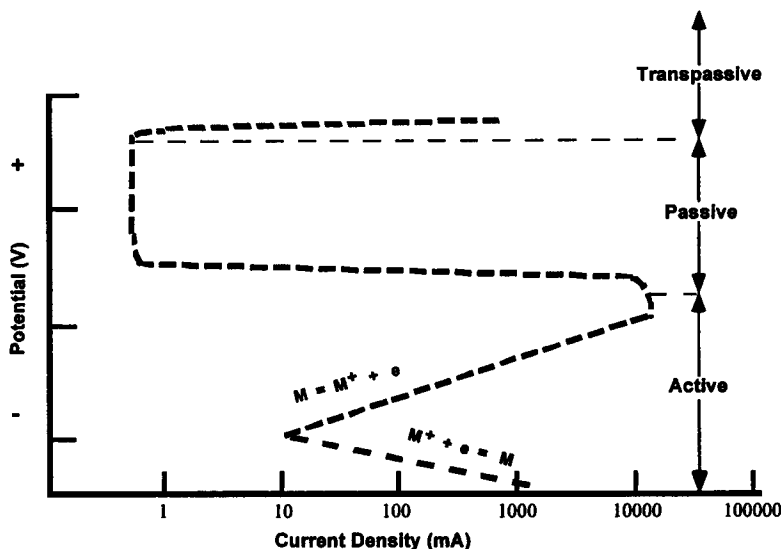


Figure 1. Theoretical passivation diagram.

iron oxides, varying amounts of ions from the passivating medium (such as Cr or phosphate) may also be present. Ligands that strongly complex with iron (EDTA, citrate, and chloride) will tend to disrupt the passive film, or make it more difficult to form.

A good method for studying passive film formation involves examining polarization curves.¹⁰ Theoretical anodic and cathodic polarization curves are shown in Figure 1. As the potential is shifted in the anodic (+) direction, the current (corrosion rate) increases. At a critical current density (I_{crit}), the current drops to a low value—indicating the onset of passivation. With the use of polarization curves, the solution conditions controlling passivation can be determined and described. Polarization curve analysis will be extensively used in the subsequent sections to describe passivation in chemical cleaning solutions.

Nonchelating Agent Passivators

These formulations frequently are used after acid cleaning treatments to leave the surfaces in a condition (called “passive”) that resists corrosion from the ambient atmosphere. Note, however, that the metal is passive in an electrochemical sense only while it is in contact with the solvent. Upon exposure to the air in the plant, passivating conditions rapidly cease to exist.

Three different common passivating systems were studied by using an electrochemical cell described in Figure 2.⁷ The anodic polarization curves were determined for mild steel in phosphate/nitrite, sodium carbonate/nitrite, and ammonia/hydrazine. These are the most commonly employed treatments for acid cleaned surfaces.

Phosphate System. This system consisted of 0.25% NaH_2PO_4 , 0.25% Na_2PO_4 , and 0.5% NaNO_2 . The system also contained dissolved air. Without air, the polarization curves did not show spontaneous passivation; however, this behavior is present with air and phosphate.

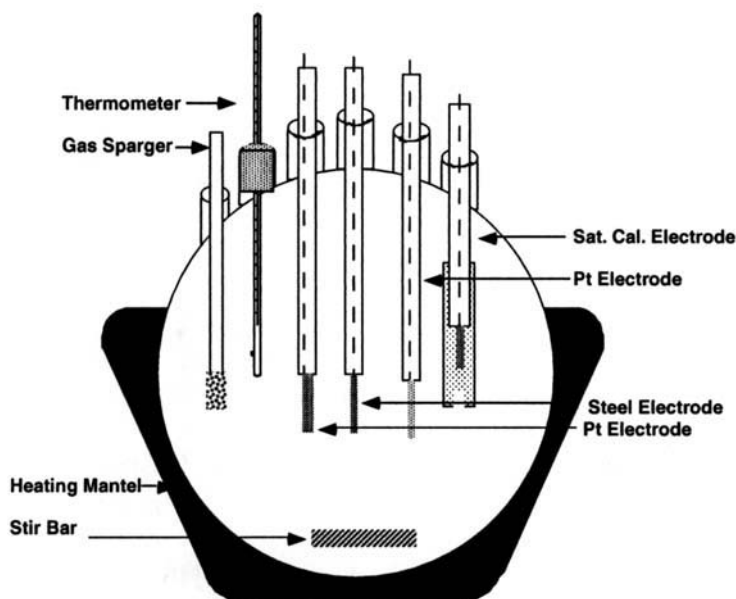


Figure 2. Passivation cell.

Sodium Carbonate. This solution consists of 1% NaCO_3 with 0.5% NaNO_2 . The polarization curves also show that this system achieves spontaneous passivation only when air is present.

Ammonia/Hydrazine. Polarization curves did not indicate spontaneous passivation; however, one specimen did develop a dark gray coating in the presence of air. The results of the exposure tests are shown in Table 1.

From these tests, only the phosphate/nitrite solutions achieved any passivation without air. All of the systems did benefit from introduction of the second oxidizer (air). Additional studies evaluated citrate/iron/nitrite (as after a Citro-Solv treatment), phosphate/hydrazine, and carbonate/gluconate/phosphate. The citrate/iron/nitrite was a very effective passivator, but the other two solutions were not as effective. The conclusion is that the more powerful oxidizers are the more effective passivating solutions.

TABLE 1
Passivation Tests⁷

Components	Temperature (°F)	Air Present	Satisfactory Passivation
Phosphate/Nitrite	150	Yes	Yes
Phosphate	150	Yes	No
Phosphate/Nitrite	150	No	Yes
Carbonate/Nitrite	200	Yes	Yes
Carbonate/Nitrite	200	No	No
Carbonate	200	Yes	Yes
Carbonate	200	No	No
Ammonia/Hydrazine	200	Yes	Yes
Ammonia/Hydrazine	200	No	No

Passivation with Iron EDTA

Ferric EDTA [Fe(III)EDTA] is generated during the oxidation stage of the iron- or copper-removal treatments described in the previous chapter, and acts as an in situ passivator. This chemical species is diffusion limited when acting as a passivator or corrodent.¹¹ An effective way to study the electrode reactions of a diffusion-limited species involves the use of a rotating disk electrode (RDE). Tobias¹² provided an excellent study of Fe in acidic ferric solutions using the RDE. The limiting diffusion current at a RDE is given by

$$I_{\text{Lim}} = 59816 D^{2/3} \nu^{-1/6} \omega^{1/2} [\text{Fe}^{3+}], \quad (1)$$

where D is the diffusion coefficient, ν is the kinematic viscosity (Stokes), and ω is the angular velocity (radians per second). The diffusion coefficient can be found by varying the rotation rate and making a plot of I_{Lim} vs. $\omega^{1/2}$. Thus,

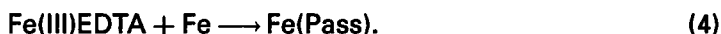
$$D = \{d I_{\text{Lim}} / d \omega^{1/2} \nu^{1/6} / 59816 [\text{Fe}^{3+}]\}^{3/2}. \quad (2)$$

D and ν vary with temperature and must be experimentally determined. At passivation, I_{Lim} should be greater than or equal to the critical passivation current (I_{Crit}). The I_{Crit} values were measured from the polarization curves of steel RDEs in $(\text{NH}_4)_4\text{EDTA}$ at various pH values, temperatures, and [EDTA]. When actual passivation experiments were conducted, I_{Lim} at passivation was also estimated. The relationship between these current densities (CDs) should reveal important information concerning the passivation reaction.

Anodic polarization curves in $(\text{NH}_4)_4\text{EDTA}$ under various conditions of pH, temperature, and $[(\text{NH}_4)_4(\text{EDTA})]$ were run with a RDE. Iron was excluded from the tests. The I_{Crit} was determined. Various concentrations of Fe(III)EDTA were prepared, and cathodic polarization curves were determined so that D could be calculated. Finally, actual passivation tests were run to relate the passivation to pH, temperature, $[(\text{NH}_4)_4\text{EDTA}]$, flow, and $[\text{Fe}^{3+}]$. The I_{Lim} was calculated at passivation and compared to I_{Crit} determined from the anodic curves. In addition, the effects of various oxidizers used to generate ferric EDTA were evaluated in short- and long-term tests. For example,



and



The iron chelate was made by refluxing 20% $(\text{NH}_4)_4\text{EDTA}$ with iron powder followed by oxidation to the Fe^{3+} state with H_2O_2 . The excess H_2O_2 was decomposed by a 5-min boil. The iron concentrate was analyzed for Fe by using an atomic absorbance (AA) spectrophotometer, and free EDTA was determined with the SrCl_2 method. Test solutions to give final [Fe] and [EDTA] were made from the concentrates and checked by AA. The final pH value at room temperature, 74°F (24°C) was adjusted with NH_4OH or HCOOH by using a digital pH meter. Ferrous chelate solutions were prepared as described above, but the solutions were reduced with N_2H_4 .

The basic equipment was a RDE made from 1018 carbon steel (CS; Figure 3) in the electrochemical arrangement in Figure 4. The rotation rate could be varied from 20 to 10,000 rpm. A jacketed glass cell held ~600 mL of solution. The cell could be purged with gas. The saturated calomel electrode (SCE) was in a separate compartment

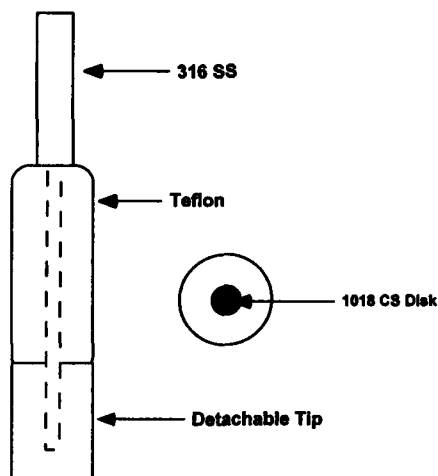


Figure 3. Rotating disk electrode.

connected to the cell with a KCl bridge and fritted glass. The potentials and currents were controlled with a potentiostat. Potentials vs. rpm were recorded on a two pen, strip-chart recorder.

Polarization Curves. The test solution was made at laboratory temperature, and the pH value was adjusted with NH_4OH or HCOOH . A total of 600 mL was thermostated

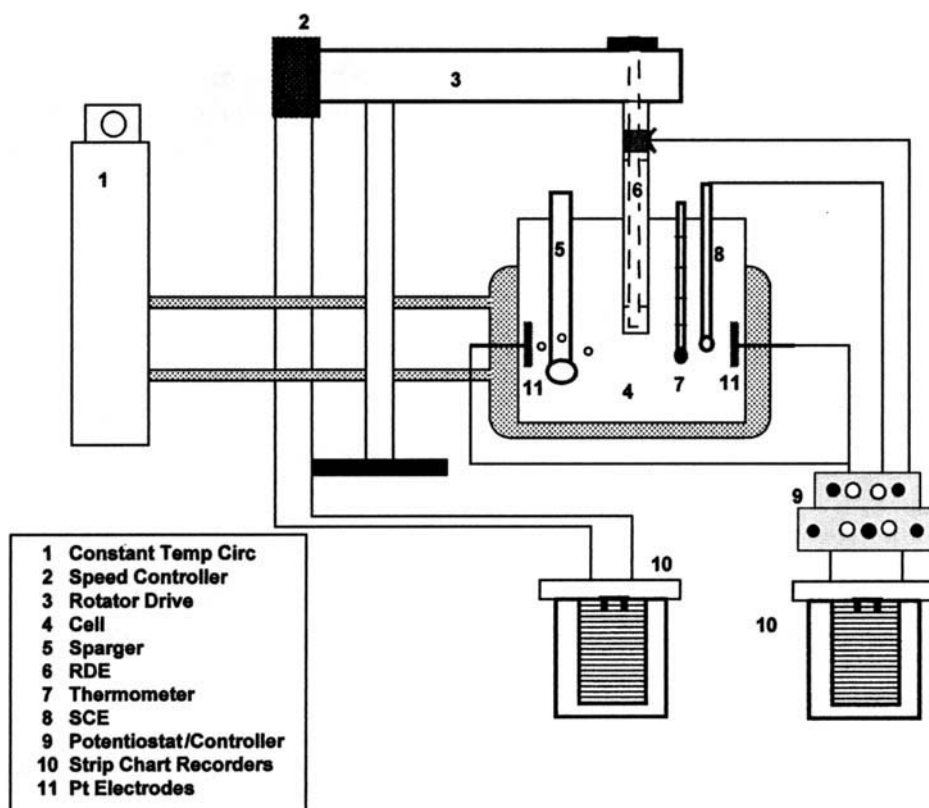


Figure 4. Passivation with RDE.

in the closed cell. At the test temperature, a sample was removed, cooled, and the pH value was rechecked at laboratory temperature. Air was not excluded in these tests. The RDE steel tip was polished to 600 grit before all of the runs and activated in boiling $(\text{NH}_4)_4\text{EDTA}$. The tip was put on the RDE and lowered into the solution, and the rotator was activated at the test rpm. The potentiostat was placed on direct reading, and the open circuit potential (OCP) was allowed to equilibrate for ~ 10 min. Anodic or cathodic scans were then run from the OCP at 2 mV/s.

The I_{crit} was determined from the anodic scans of the iron RDE in iron-free EDTA solutions. The I_{crit} value reported is the average of runs at three to five different rpms. The cathodic curves of Fe(III)EDTA at various iron concentrations allowed a calculation of D at three temperatures. The kinematic viscosity was measured at three temperatures by using a bulb viscometer.

Passivation rpm. According to the first definition of passivation, a metal is passive when it behaves like a noble metal. In these iron EDTA solutions, a noble metal such as Pt measures the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of the solution.⁴ From experience, the emf measured (Pt vs. SCE) in solutions containing predominantly Fe(III)EDTA will be more positive than -100 mV. The active steel usually exhibits an OCP (Fe vs. SCE) value of approximately -800 mV. When the steel passivates, the OCP will increase by several hundred millivolts and will eventually reach ~ 100 mV. To conduct the experiment, the polished active RDE was lowered into the heated prepared Fe(III)EDTA solution. Beginning from 0 rpm, the rotation rate was slowly increased until the steel emf suddenly rose to approximately -300 mV. The emf and rpm were recorded on the two-pen recorder. The passivation rpm was determined from the chart recorder traces. A typical trace is shown in Figure 5. The x axis reflects chart movement or time to passivation, but the time factor was not studied. The tests were repeated three to five times, and the rpm (pass) was averaged. A number of graphical relationships between $[\text{Fe}^{3+}]$ rpm, free EDTA, and temperature were derived from these data. In addition, with the use of the values of D calculated above and Equation (2), I_{Lim} at passivation was calculated.

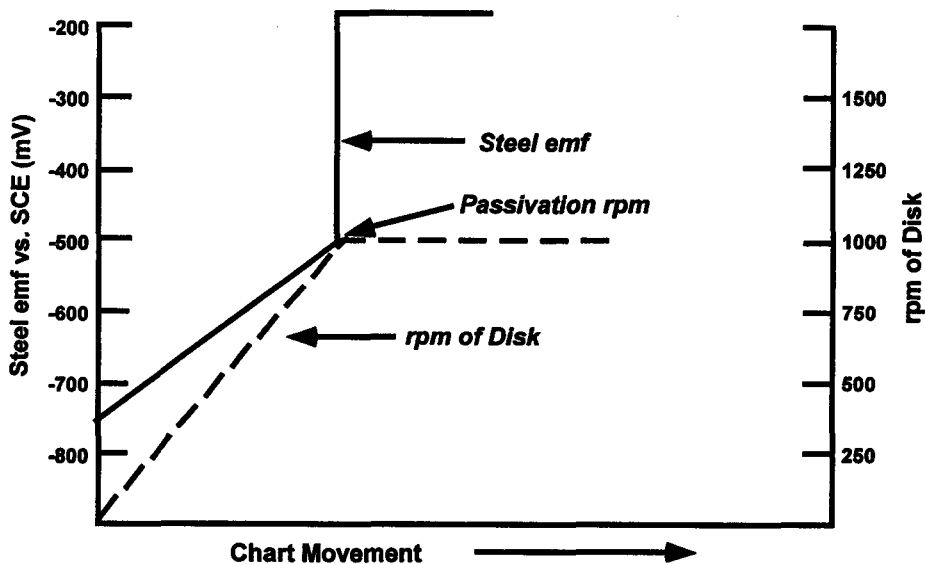


Figure 5. Steel emf and disk rpm test.

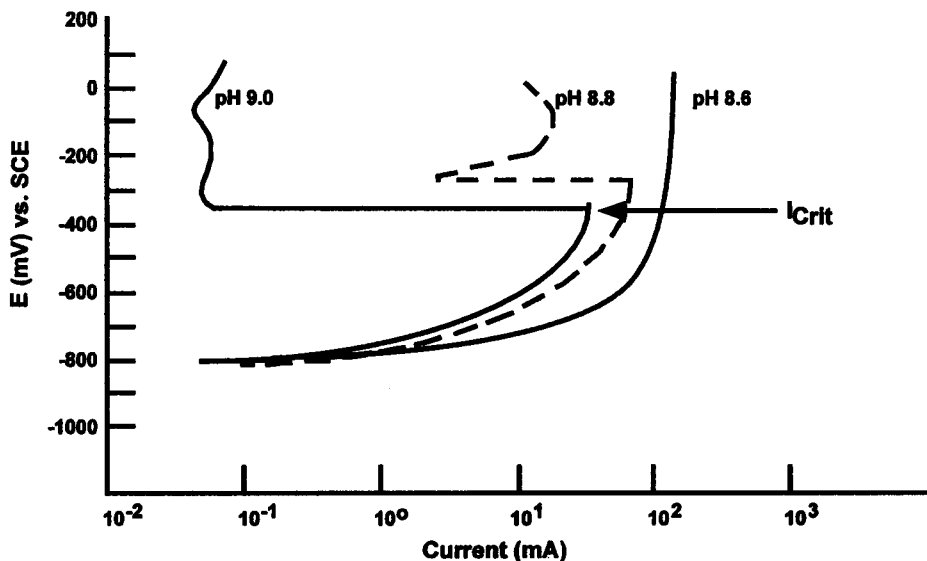


Figure 6. Anodic polarization curves in ammonium EDTA.

Anodic Polarization Curves in Pure EDTA. Anodic curves were determined for two $(\text{NH}_4)_4\text{EDTA}$ concentrations and three temperatures. A typical trace is shown in Figure 6. Excellent active/passive behavior is seen, and I_{Crit} is easily determined. The passivation potential is approximately -300 mV; Table 2 is a list of the I_{Crit} values at a pH of 9.3. As expected, the critical CD for passivation increased with temperature and free EDTA concentration. The active corrosion CDs before achieving passivation are quite high, so I_{Crit} must be exceeded as rapidly as possible.

The effect of the pH was studied by lowering the pH value with formic acid. Three anodic curves are shown in Figure 6. Not only is I_{Crit} increased as the pH value drops, but the passivation region is distorted. By a pH of 8.6, there is no passivation region in pure EDTA. As will be seen in later sections, other factors influence passivation at the lower pH values.

Cathodic Curves with Fe(III)EDTA. Cathodic curves in the presence of Fe(III) EDTA were run at five iron concentrations and three temperatures. The major goal was a calculation of D at the three temperatures. A sample of the cathodic curves

TABLE 2

I_{Crit} Values in EDTA (pH of 9.0)

Temperature ($^{\circ}\text{C}$)	I_{Crit} (mA/cm 2)
0.8% $(\text{NH}_4)_4\text{EDTA}$	
54	8.0
65	13.2
77	20.3
1.6% $(\text{NH}_4)_4\text{EDTA}$	
54	16.2
65	24.8
77	45.3

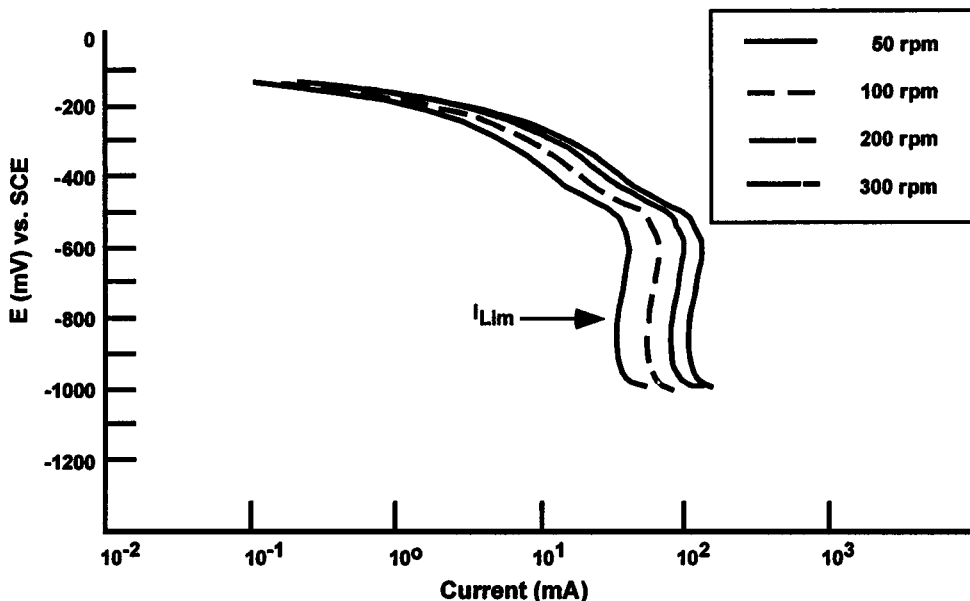


Figure 7. Cathodic polarization curves in ferric EDTA.

is seen in Figure 7. The expected diffusion-controlled nature of the reduction $[\text{Fe(III)EDTA}^- \rightarrow \text{Fe(II)EDTA}^{2-}]$ is confirmed by these graphs. Tobias¹² measured D for Fe^{3+} in H_2SO_4 to be $5.2 \pm 0.3 \times 10^{-6} \text{ cm}^2/\text{s}$ at 77°F (25°C). Because the coefficient should increase as the temperature increases, the present values ($7.5 \pm 2.5 \times 10^{-6} \text{ cm}^2/\text{s}$) are in reasonable agreement with the literature, and they should increase our confidence in the RDE technique.

Passivation Tests. As described above, a large number of tests were run to determine the rpm at which passivation occurs. From Equation (2), plots of $\omega^{1/2}$ or its equivalent, $(\text{Re}^{1/2})$ vs. $[\text{Fe}^{3+}]$, should yield a straight line at a given temperature.

$$\text{Re(RDE)} = r^2 \omega / \nu. \quad (5)$$

However, this is not a very convenient form of display for comparisons. Therefore, the passivation Re vs. $[\text{Fe}^{3+}]$ on a semilog plot is shown in Figure 8. These curves allow a better pictorial sense of the relationships between (Re) , $[\text{Fe}^{3+}]$, $[\text{EDTA}]$, and temperature to the passivation of steel. As noted earlier (Figure 6), the pH has a pronounced effect on passivation. In uncontaminated EDTA, the passive region disappears by a pH of 8.6. The RDE passivation tests were run at a pH of 8.75, 8.3, and 7.3, as well as at 9.3, in solutions containing 0.8% free EDTA, and an emf change indicating the onset of passivation was observed at a pH as low as 7.3. However, very high rotation rates were required. Therefore, while passivation may be possible at lower pH values, the very high critical CD's required probably limit the usefulness of the system to pH levels of ± 9.0 .

The effect of a pH value was also studied in the presence of 3600 ppm Fe^{3+} and 0.8% free EDTA, using full polarization curves. To initiate the scan from the active state, the electrode was not rotated. In the presence of the added iron, a single cathodic loop corresponding to the reduction of Fe^{3+} to Fe^{2+} is seen at a pH of 9.3. The onset of passivation occurs at -300 mV , and the CD in the passive region is $\sim 20 \mu\text{A}/\text{cm}^2$. At a pH of 8.0 (with Fe^{3+}), two cathodic loops are present, corresponding to the reduction

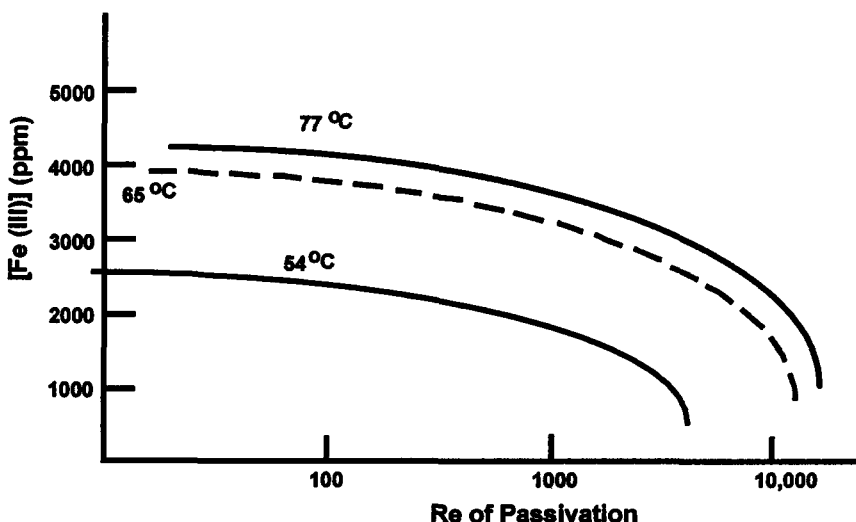


Figure 8. Reynolds number (Re) of passivation.

of Fe^{3+} as well as H^+ . Evidence for the onset of passivation (at -300 mV) exists because the anodic CD is about 10-fold lower than the active (cathodic) CD. In the absence of ferric ions (Figure 5), the passive region does not exist below a pH of 8.6. At a pH of 7, the current resulting from H^+ reduction is increased, and little evidence of passivation exists (corrosion CD of $\sim 1000 \mu\text{A}/\text{cm}^2$).

The data demonstrate the significant relationships between (Fe^{3+}), (EDTA), temperature, flow rate, and pH. Passivation is most easily achieved at (1) high flow rate, (2) high iron concentration, (3) low free-EDTA concentration, and (4) low temperature. For a practical application of this technology to the cleaning of steel, ferric EDTA must be generated from the ferrous EDTA available at the end of the iron-removal stage. A definitive kinetic study of the reaction, oxidant + $\text{Fe(II)EDTA} \rightarrow \text{Fe(III)EDTA}$, has not been made. However, at a constant aeration, the relative rates are $\text{H}_2\text{O}_2 > \text{air} + \text{NaNO}_2 > \text{air} > \text{NaNO}_2$. Martell¹³ determined the absolute half-life for the reaction between O_2 and Fe(II)EDTA to be 0.11 s at 77°F (25°C) and a pH of 9.3.

Thus, mass transport effects control the effective rate of ferric generation for air. In situations in which the introduction and distribution of air are limited, the use of the more vigorous oxidants such as H_2O_2 or $\text{air} + \text{NaNO}_2$ is strongly indicated so that the correct amount of ferric can be generated and i_{Crit} is surpassed in a minimum amount of time. Until i_{Crit} is achieved, the equipment being cleaned will experience very high corrosion rates.

As stated earlier, i_{Lim} should be $> i_{\text{Crit}}$ at passivation. The critical CDs have been measured from the anodic polarization curves and are shown in Table 3. i_{Lim} at passivation was calculated by using Equation (2). The calculated i_{Lim} values along with the observed i_{Crit} values are listed in Table 4. At 0.8% $(\text{NH}_4)_4\text{EDTA}$, the observed limiting diffusion currents are significantly lower than i_{Crit} at the higher (Fe^{3+}). A similar trend can also be seen at 1.6% $(\text{NH}_4)_4\text{EDTA}$, but the effect is not as pronounced as that at 0.8% $(\text{NH}_4)_4\text{EDTA}$. At 171°F (77°C)/1.6% $(\text{NH}_4)_4\text{EDTA}$, the limiting currents are significantly higher than i_{Crit} . If the only role of ferric EDTA was as a cathodic depolarizer, supplying a source of CD to maintain passivation, i_{Lim} should not vary with

TABLE 3

Limiting Diffusion Current at Passivation and Critical Passivation Currents (mA/cm²)

0.8% (NH ₄) ₄ EDTA							
Fe Conc. (ppm)	129 °F (54°C)		149 °F (65°C)			171 °F (77°C)	
	<i>I</i> _{Crit}	<i>I</i> _{Lim} Pass	<i>I</i> _{Crit}	<i>I</i> _{Lim}	Pass	<i>I</i> _{Crit}	<i>I</i> _{Lim} Pass
	8.0		13.2			20.3	
800		8.8		12.5			27.7
1680		7.0		11.9			35.2
2700		–		11.4			15.8
3600		–		9.5			9.2
4100		–		5.5			–

1.6% (NH ₄) ₄ EDTA							
Fe Conc. (ppm)	129 °F (54°C)		149 °F (65°C)			171 °F (77°C)	
	<i>I</i> _{Crit}	<i>I</i> _{Lim} Pass	<i>I</i> _{Crit}	<i>I</i> _{Lim}	Pass	<i>I</i> _{Crit}	<i>I</i> _{Lim} Pass
	16.2		24.8			45.3	
1680		20.3		23.9			59.7
2700		18.1		29.0			68.0
3600		14.7		24.0			50.0
4100		15.0		25.0			59.0

iron concentration. This conclusion is required by Equation (2). Clearly, the iron EDTA also is changing the *anodic* reaction: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$.

This effect is seen even more clearly when the pH value is lowered below 9.0. The anodic polarization curves (Figure 6) predict that passivation is not possible below a pH of 8.6. However, the passivation of steel at pH values as low as 8.0 has been demonstrated. Hausler¹⁴ inferred that EDTA forms an *interphase* inhibitor layer on steel composed of some sort of insoluble FeEDTA complex. Such a complex layer would change the iron dissolution kinetics and also possibly influence the passivation behavior. As the free-EDTA concentration increased, this layer would tend to be less stable. The present data confirm such a trend.

The treatment of the surfaces with ferric EDTA allows the solvent to dissolve any copper plated onto the steel surfaces and leaves the cleaned metal in a “passive” condition similar to those generated by the other alkaline oxidizers described above.

CHEMICAL CLEANING INHIBITORS

The majority of equipment requiring cleaning is constructed of iron-base alloys such as carbon and alloy steels, or copper alloys. These metals will be attacked by the aggressive solvents (mineral acids, organic acids, and chelating agents), unless the cleaners contain corrosion inhibitors. An uninhibited solvent would damage the equipment being cleaned and the corrosion would consume the expensive solvent. Thus, without the use of corrosion inhibitors, most chemical cleaning operations could not be performed.

The technology of acid corrosion inhibition was reviewed by Riggs,¹⁵ and applications to chemical cleaning processes were reviewed by Oakes¹⁶ in 1972. Also

refer to the excellent reviews in the European Federation of Corrosion's Publication 11.¹⁷ It is the purpose of this section to review advances in corrosion inhibition technology that are applicable to chemical cleaning solvents, and that appeared in the literature since the early 1970s. For clarity, a few earlier references also are included. Chemicals and processes that were used with mineral acids are discussed, as well as those with organic acids and chelating agents. Special problems that include ferric ion corrosion and cleaning of alloys unique to steam-generating equipment also will be reviewed. The technology of chemical cleaning will be considered only as far as there are implications for inhibition and corrosion control. The major emphasis will be on inhibitors designed to protect iron and steels. This is not intended to be an exhaustive review; rather it is a sampling of the most important recent corrosion inhibition technology. For more general information on chemical cleaning science and technology, the reader is referred to NACE TPC Publication 6,¹⁸ the EPRI manual,¹⁹ and the NACE Chemical Cleaning Manual.²⁰ Additional information on inhibitors is included in the compilations of Robinson²¹ and Rozenfeld.²² The reader also is directed to the review by Frenier and Growcock.²³

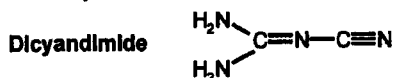
Inhibitors for Mineral Acids

Acid cleaning of water-formed deposits in boilers originated from technology used in the stimulation of oil wells. Likewise, acid corrosion inhibition technology was first developed there, and contributions from oilfield applications continue to be significant. Acid pickling operations are closely related, too, as is the inhibitor technology; indeed, many of the recently published studies of acid corrosion inhibition fall in the realm of acid pickling. Developments over the past two decades that are pertinent to all three industries are described and reviewed in several publications. Olbertz²⁴ explored various facets of steel corrosion inhibition and hydrogen absorption by steel in hydrochloric acid (HCl). He describes some extensive mechanistic research on mixtures of propargyl alcohol and quaternary nitrogen salts as well as a large number of individual quats, aldehydes, and ketones. He also provides an extensive compendium of inhibitors for hydrogen absorption, especially developments in the Soviet Union, through 1979. Sanyal²⁵ gave a historical account of corrosion inhibitors, also through 1979, that classifies organic inhibitors for iron dissolution as follows: amines and imines, sulfur compounds, onium compounds, and unsaturated compounds containing double and triple bonds. Finally, in an excellent review of the acid corrosion inhibitor field through 1982, Schmitt²⁶ described organic inhibitors used in the three industries: primarily nitrogen compounds and acetylenics and, to a lesser extent, sulfur compounds for HCl, HF, and H₃PO₄; sulfur compounds and, to a lesser extent, acetylenics for H₂SO₄; and sulfur compounds for HNO₃.

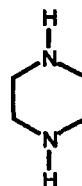
Hydrochloric acid is the solvent most often used for chemical cleaning applications, because it is economical to use and attacks a wide range of scales. More than 100 papers on organic corrosion inhibitors for steel or copper in HCl have appeared in print since 1970. The majority of these are represented here. However, the main concern here is the inclusion of all the major classes of compounds, which we have organized by hetero-atom: nitrogen, phosphorus, and so on. The chemical structures of some of these are given in Figure 9.

Nitrogen compounds constitute the largest class of inhibitors for HCl. These can be very effective at moderate temperatures, that is, <149°F (<65°C), and acid

N Compounds



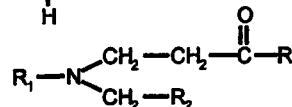
Piperazine



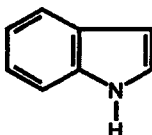
Pyrrole



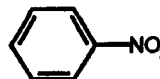
Rosin amine
Mannich product
(R_1 = alkylyl)



Indole

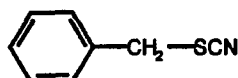


Nitrobenzene

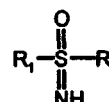


S/N Compounds

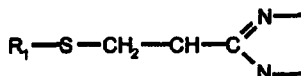
Benzyl thiocyanate



Sulfoximine



Product of a
Thiol with a nitrile

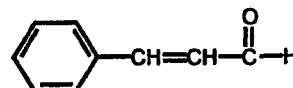


O Compounds

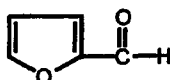
Crotonaldehyde



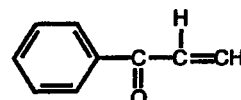
Cinnamaldehyde



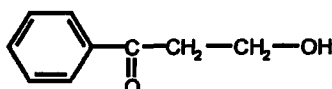
Furfural



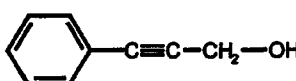
Phenyvinyl ketone



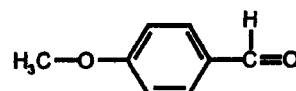
β -Hydroxypropioophenone



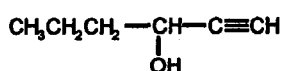
3-Phenyl-2-propyn-1-ol



p-Anisaldehyde



Hexynol



Ethyl octynol

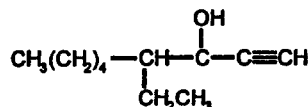


Figure 9. Inhibitors for HCl.

concentrations (<15 wt. % HCl). Subramanyan et al.²⁷ studied a variety of amines (aromatic and aliphatic) and triazoles in various acids, including HCl, and found them to be highly effective. In a study of polymethylene imines and diamines, Aramaki et al.²⁸ discovered that the inhibition was due to the formation of polymers. Nametkin et al.²⁹ reported that propylene diamine is also effective. Alfandry et al.³⁰ claimed that hexamine is effective even in the presence of Fe^{3+} , and Dhirendra and Sanyal³¹ showed that hexamine works well even on AISI 321 SS. Willars et al.³² found a variety of

alkylamines that are effective on mild steel, but urotropine (hexamine, AKA hexamethylenetetramine), which is widely used in spite of its propensity to form the carcinogen bis-chloromethyl ether,³³ is probably the most effective of all the alkyl amines.

Amides can also be very effective inhibitors. For example, dicyandiamide³⁴ provides steel with >90% protection in 4% (1N) HCl (also in H₂SO₄) up to at least 129°F (54°C). Nitriles, such as cinnamionitrile,³⁵ are good inhibitors for both iron dissolution and hydrogen absorption, but they are not widely used. In contrast, imidazolines are popular. Kataoka and Takada³⁶ filed patents on various imidazoline derivatives, and Patel et al.³⁷ found that benzimidazoles are effective for copper and brass in HCl. A combination of amino and azo groups seems to work very well. For example, D'Errico³⁸ discovered that dialkylaminomethyl aromatic triazoles are effective in 5% HCl at 171°F (77°C).

Aromatic nitrogen salts were extensively investigated. Halides of *n*-alkyl pyridine,³⁹ *n*-alkylbenzylpyridine (Katapin in the Soviet Union),⁴⁰ *n*-alkylisoquinoline,⁴¹ and alkylbenzylquinolines⁴² are all highly effective steel corrosion inhibitors. Most of these compounds are not only excellent inhibitors for iron dissolution, but also for hydrogen absorption, and they appear to work well even in the presence of H₂S. Recently, Schmitt and Bedbur⁴³ systematically tested several pyridinium and quinolinium derivatives on iron and steel in deaerated 10% HCl; the best corrosion inhibitor was found to be *l*-naphthylmethylquinolinium chloride. Interestingly, none of the inhibitors performed as well on carbon steel as on iron. Phosphoniums can also perform well, as evidenced by Sanyal and Srivastava's work on phenyl benzylphosphonium chloride.⁴⁴

Most of the important oxygen compounds have unsaturated groups. The vast majority of these are acetylenic alcohols (α -alkynols), which are widely known for their superior performance at elevated temperatures. Many recent studies of acetylenic alcohols were conducted in H₂SO₄ or with mixtures of the acetylenics and various nitrogen or sulfur compounds (see below), but work on acetylenic alcohols per se in HCl has also continued. Tedeschi and co-workers⁴⁵ developed an assortment of highly effective aliphatic acetylenic alcohols. Growcock et al.⁴⁶ and Growcock and Lopp⁴⁷ studied phenyl propynols. Generally, the aromatic acetylenics appear to be just as active as their aliphatic counterparts, but they also react with HCl. However, the products so formed are themselves active inhibitors and perform especially well in the presence of surfactants.

Rzaeva et al.⁴⁸ compared propargyl ether, propargyloxy formates, and propargyloxy acetates, and found them all to be effective inhibitors of steel in HCl. Allabergenov et al.⁴⁹ synthesized various propargyl ethers of substituted phenols, which also proved to be quite effective (18% HCl at 160°F, i.e., 71°C). One such product, 1-phenoxy-2-butyne-4-ol, is so exceptional that it has been the subject of subsequent studies.⁵⁰

Other oxygen compounds that have been investigated in a study⁵¹ include pyrole, indole, and their dimethyl derivatives. These compounds not only inhibit the corrosion of steel relatively well, but they also accelerate the rate of the dissolution of magnetite; however, in that study, the magnetite and steel were not coupled, so it is difficult to surmise what the effect might be on magnetite-covered steel. The α,β -unsaturated aldehydes and α -alkenylphenones were also investigated. Of the aldehydes, aromatic species such as cinnamaldehyde are the best. Several aromatic aldehydes were investigated by Devarajan and Balakrishnan in four mineral acids,

including HCl.⁵² Growcock and Frenier⁵³ observed high levels of protection when the aldehydes were used with a surfactant, such as an ethoxylated phenol or alkanol. The best results were obtained with a quaternary nitrogen salt as the surfactant. Frenier et. al.⁵⁴ discovered that benzoylallyl alcohol, one of the simplest α -alkenylphenones, is a superior inhibitor in both 15% and 28% HCl; furthermore, on exposure to the acid, several seemingly unrelated compounds, such as 5-benzoyl-1,3-dioxane and *p*-hydroxypropiophenone, convert to the alcohol. Surfactants enhance the inhibition, particularly in 28% HCl.

Sulfide-containing scales pose a special problem for acid cleaning. Dissolution of the sulfide inclusions releases H₂S, which reacts with the steel and charges it with hydrogen.⁵⁵ In high-strength steels, this can lead to hydrogen embrittlement. Frenier³³ and Frenier et al.⁵⁶ found that aldehydes added to the acid can virtually eliminate H₂S evolution and the accompanying corrosion.

Maskow et al.⁵⁷ found that aromatic sulfides are generally much more effective than aliphatic sulfides, but, in most cases, neither works very well at HCl concentrations above 10%. However, dipropargyl sulfide is one of the best, if not the best, single inhibitor ever discovered for steel in HCl.⁵⁸ It is very effective over wide ranges of temperature and acid concentration. Mercaptans (thiols) are also excellent steel corrosion inhibitors; indeed, they received considerable attention in the 1950s and 1960s. Since then, interest in them has waned, perhaps as a result of their odoriferous and toxic nature and their tendency to form H₂S in situ.

Thiourea also was the subject of many earlier studies. Most current work with thiourea or its derivatives is with mixtures (see below). Studies with pure thiourea indicate that when used at moderate concentrations, it inhibits the corrosion of steel and copper in most mineral acids, but at high concentrations it accelerates the attack.^{59,60} Thiourea derivatives are much more effective than thiourea itself. In particular, phenyl thiourea was found to be very good for copper and brass in HCl at concentrations up to 25% (7 N).^{61,62} It is also a reasonable inhibitor for steel, but, like H₂S and the mercaptans, it can promote hydrogen absorption.⁶³ Pillai and Narayan⁶⁴ studied various nitrogen and sulfur-substituted thioureas on iron in HCl, for example, ethylene thiourea vs. sulfur-benzylisothiurea, and discovered that the sulfur-substituted derivatives show increasing effectiveness with increasing inhibitor concentration. The sulfur-substituted thioureas are generally safe inhibitors because, in contrast to the nitrogen-substituted derivatives, they do not increase the rate of H₂ evolution. Studnicki⁶⁵ synthesized various derivatives of alkylarylamines and determined from H₂ evolution measurements that isothiurea derivatives are superior to imidazole or amine structures for stainless steel in 36% (or 40%) HCl and for mild steel in 18% H₂SO₄ at 122°F (50°C). In addition, the high performance of the isothiurea derivatives can last for several days. In a similar vein, Thompson et al.⁶⁶ discovered a family of aminoalkylsulfur compounds that all gave in excess of 90% protection to AISI 1020 steel (1-h tests conducted in 10% HCl at 171°F, i.e., 77°C, and 10% H₂SO₄ at 190°F, i.e., 88°C).

Ateya et al.⁶⁷ tested thiosemicarbazide and Pevneva et al.⁶⁸ examined pyrazolene derivatives; both types of compounds worked well in HCl at low concentrations. Methylene Blue (3,9-bisdimethylaminophenazothionium chloride) is another efficient inhibitor.⁶⁹ Aliphatic and aromatic thiocyanates work well on steel in HCl.⁷⁰ Here again, caution must be used when alloyed steels are cleaned; as with many other

sulfur compounds, thiocyanates can degrade to form H_2S , which accelerates hydrogen embrittlement.

Many designed inhibitors are the products of attempts to blend the good qualities of different inhibitors into single compounds that perform better and can be quality controlled better than formulations.

Unsymmetrical sulfoximines containing at least one long alkyl chain were found to be effective on most steels in various nonoxidizing acids (especially HCl and H_2SO_4) at concentrations up to 30% and temperatures up to at least 203°F (95°C).⁷¹ Ethoxylated surfactants improve inhibitor effectiveness. Derivatized sulfoniums can be very efficient inhibitors, as in the case of nitrifluorobenzyl dodecylmethylsulfonium chloride.⁷²

Rozenfeld⁷³ investigated hetero-alkylated amines and urotropine hydroiodide, and found them to be more effective than the unsubstituted amines. Chlorinated amines were also investigated by Tamura et al.⁷⁴ Recently, Tagmazyan et al.⁷⁵ discovered that alkyl(2-hydroxyethyl)dimethylammonium bromides are effective corrosion inhibitors for steel in HCl . Aldoximes and ketoximes can also be very effective, according to Costain and Terry.³⁵

Condensation products of aryl amines, such as aniline, with formaldehyde (and larger aldehydes as well) are quite effective,^{76,77} as are the condensation products with various large ketones⁶³ (the Soviet inhibitor PB-8t2 is similar). Mannich bases,⁷⁸ which are condensation products of an amine, an aldehyde, and a ketone, can be very good even at temperatures in excess of 203°F (95°C); see Equation (1). Schiff bases, which are condensation products of an amine and an aldehyde, e.g., aniline plus benzaldehyde, can be quite good as well.⁷⁹

Nitro compounds were also a subject of interest. Aramaki⁸⁰ examined 11 ring-substituted nitrobenzene derivatives as inhibitors of iron in 20% (6 N) HCl at 86°F (30°C), and found that they accelerated the cathodic reaction but suppressed the anodic reaction. The nitro compounds not only can donate electrons to the metal, but they can also accept electrons in their antibonding π orbitals; thus, the nitro compounds may bond more strongly to the surface than corresponding amines that are not able to accept backbonding from the metal.

Derivatives of acetylenic alcohols, such as 1-iodo-3-methyl-1-butyn-3-ol,⁴⁵ are some of the most efficient inhibitors for HCl , especially at elevated temperatures. Alkynoxymethyl amines combine the properties of amines and acetylenic alcohols into a single compound.⁸¹

Natural products were the subject of additional study, especially in developing countries. Kumar et al.⁸² tested gelatin (a polypeptide composed primarily of glycine, proline, and hydroxyproline) as a steel corrosion inhibitor in HCl , and found it to be quite effective at moderate acid concentrations and temperatures. Surprisingly, gelatin lowers the apparent activation energy of the corrosion reaction, as well as the rate; with an inhibitor loading of 1%, levels of protection remain high (80–94%), even at acid concentrations as high as 32%.

The frontiers of corrosion inhibitor technology are being pushed in directions that involve molecular design with exotic combinations of functional groups. One example is dihydronitrogen heterocyclic phosphoramidates. These compounds, which contain a double-bonded ring of nitrogen and a $\text{P}=\text{S}$ bond, appear to be quite effective for steel in HCl over a wide range of acid concentration.⁸³ Likewise, compounds

containing both amino (or amido, cyclic amidine, or epihalohydrin-derived amino) and mercapto groups⁸⁴ or compounds containing both C=S and P=O moieties along with C=C unsaturation⁸⁵ also are effective inhibitors.

Nitrogen compounds and acetylenic alcohols are often used together to give high levels of protection at elevated temperatures and high acid concentrations. One very effective mixture, which supposedly is effective on zinc as well as on steel and copper, consists of N,N'-dicyclohexylthiourea, ethynylcyclohexanol, and polyaminomethylene phosphonate.⁸⁶ Nichols et al.⁸⁷ patented a similar mixture consisting of a heterocyclic nitrogen compound, an acetylenic alcohol, and a dialkylthiourea. Mixtures of quaternary nitrogen salts, imines, thiourea derivatives, and acetylenic alcohols are often used with good results, and Mannich bases mixed with acetylenic alcohols are also quite effective.

The performance of amine-base inhibitors can be substantially improved by metal halides, especially CuI.⁸⁸ Urotropine was used for years in mixtures with Sb³⁺ and/or Cu²⁺ salts or KI (the Soviet inhibitors SU, SUM, U-1, and UM series).²⁴ Walker⁸⁹ discovered that a mixture of an acetylenic alcohol, an aromatic nitrogen salt (quaternary ammonium compound), an aromatic hydrocarbon, and an antimony salt are very effective on ferrous metals in 15% HCl, at 500 psig (where 1 psi = 6.895 kPa), at 325°F (163°C); he claims this mixture will work well up to 500°F (260°C).

Where magnetite and copper are codeposited, a mixture of HCl and thiourea derivatives or hexahydropyrimidine-2-thione is a good solvent; the thione serves to complex the copper ions and prevent redeposition.²⁶ Likewise, a mixture of furfural and dialkylthiourea works well on galvanized or steel pipe;⁹⁰ addition of benzylthiocynate to the mixture makes it useful for steel or copper.⁹¹

Sanyal and Srivastava⁴⁴ showed that KI and phenyl benzyl phosphonium chloride act in a synergistic manner. In other work, they showed that dibenzylsulfoxide and furfuraldehyde performed very well in 6% HCl at 174°F (79°C).

Subramanyan et al.⁹² tested a variety of mixed inhibitors for corrosion inhibition and suppression of hydrogen permeation through steel. Natural substances such as alkali-treated molasses appeared to work well, too. Saleh et al.⁹³ found that aloe leaves and peels from oranges, mangoes, and pomegranates gave adequate protection to steel in 5% and 10% HCl at 77°F (25°C) and 100°F (38°C). Srivastava and Srivastava⁹⁴ reported that tobacco, black pepper, castor oil seeds, acacia gum, and lignin performed under similar conditions. Zucchi and Omar⁹⁵ tested a variety of plant extracts and obtained 88–96% protection of mild steel in 4% HCl and only slightly less protection in 8% HCl. Waste products from the coal tar industry were popular for years (known as IK-10 and KKh in the Soviet Union), and they can be very effective inhibitors of steel corrosion in HCl. However, the carcinogenic nature of some of the components led to a gradual decline in their use.

Silica and silicate deposits cannot be removed with HCl.⁹⁶ Where such scales are a problem, hydrofluoric acid is used either alone or in conjunction with HCl (or other acids). In the latter case, the HF is usually generated in situ by means of the addition of NH₄HF₂. The HCl/HF mixture has the added features of being more aggressive toward iron scales and reducing base metal corrosion by Fe³⁺ in magnetite and hematite deposits, a result attributable to the formation of a strong complex between HF and Fe³⁺.⁹⁷ For additional discussion, see the section on ferric ion corrosion.

Generally, inhibitors effective for HCl are also effective for HF. The chemical structure of a few HF inhibitors is given in Figure 10. Excellent inhibitors specifically

developed for HF include a condensation product of urotropine and a mixture of diethylthiourea and dibutyl thiourea.⁹⁸ At acid concentrations up to 10%, dibenzyl sulfoxide, alkyl pyridinium salts, di-orthotolylthiourea, and benzotriazole are highly effective.⁹⁹ Mixtures of thiourea and a Mannich base, preferably obtained from the condensation of rosin amine with acetophenone, acetone, and formaldehyde, are recommended not only for HF or HCl/HF, but also for mixtures of HF and HNO₃.¹⁰⁰ The thiourea makes all these solvents quite versatile; not only does thiourea act as a corrosion inhibitor, but also as a copper complexing agent to enhance dissolution of copper oxides and prevent replating. However, its use is limited to low acid concentration and low temperature, where its performance is optimal.

The most effective inhibitors for low-alloy chromium steels in HF are sulfur-containing compounds.¹⁰¹ These include phenylthiourea, 2-mercapto-benzimidazole, and dibenzylsulfoxide. The latter also suppresses hydrogen absorption, whereas phenylthiourea accelerates it.

Years ago, sulfuric acid (H₂SO₄) was the acid most widely used for pickling operations. However, it was not as cheap as HCl, nor recyclable. Also, scales formed in aqueous media frequently contain CaCO₃ (which reacts with H₂SO₄ to form insoluble CaSO₄).²⁰ Thus, the utility of H₂SO₄ in chemical cleaning was always limited. With the advent of alloyed steels, however, Cl⁻ induced stress corrosion cracking became a major problem, and the chemical cleaning industry was forced to seek alternatives to HCl. H₂SO₄ and phosphoric acid (H₃PO₄) are two such options. Concentrated H₂SO₄ (up to 98%) is used, sometimes in combination with HNO₃, to remove organic deposits. This solvent is quite dangerous to handle, and few organic inhibitors are stable in such a strong oxidizing environment. Indeed, inhibitors are generally used only in <15% H₂SO₄. A few chemical structures of inhibitors used in H₂SO₄ are shown in Figure 10. Whereas nitrogen compounds dominate the inhibitor field for HCl, sulfur and sulfur/nitrogen compounds are the most prevalent for H₂SO₄. A common inhibitor formulation for cleaning with H₂SO₄ contains an aromatic nitrogen salt, e.g., benzylquinolinium chloride, in combination with an acetylenic alcohol and a sulfur-containing compound of one of the following families: sulfoxide, sulfide, mercaptoimidazole, or thiourea.

Sulfoxides and sulfides received some attention in the past few years especially with regard to their inhibition mechanisms. Thibault and Talbot¹⁰² examined aliphatic sulfoxides and found they form films that aid in the inhibition. Thiophene, a cyclic sulfide, can adsorb in Temkin fashion and bring about a significant reduction in the rate of H₂ evolution.¹⁰³

Altekar et al.¹⁰⁴ found that thiourea and thio compounds decreased hydrogen absorption by carbon steels in 5% H₂SO₄ at 106°F (41°C), and Alshkel et al.¹⁰⁵ examined various heterocyclic thiourea derivatives recently in 5–18% H₂SO₄. Workers in the Soviet Union were also actively studying thiourea.^{106,107} Alfandry et al.¹⁰⁸ studied phenylthiourea inhibition of a low-alloy steel in 9% (2N) H₂SO₄ at 120 and 160°F (49 and 71°C) and found that although it gives high levels of protection, it also produces considerable pitting.

Other sulfur-containing compounds were investigated, particularly sulfonium derivatives. Sulfonium compounds can be highly efficient inhibitors for both H₂SO₄ and HCl,^{109,72} but they generally have poor thermal stability; therefore, they are used only at low temperatures. Thiosemicarbazide and thiosemicarbazone derivatives were tested over the temperature range 77–140°F (25–60°C) in 1% (0.2N) H₂SO₄

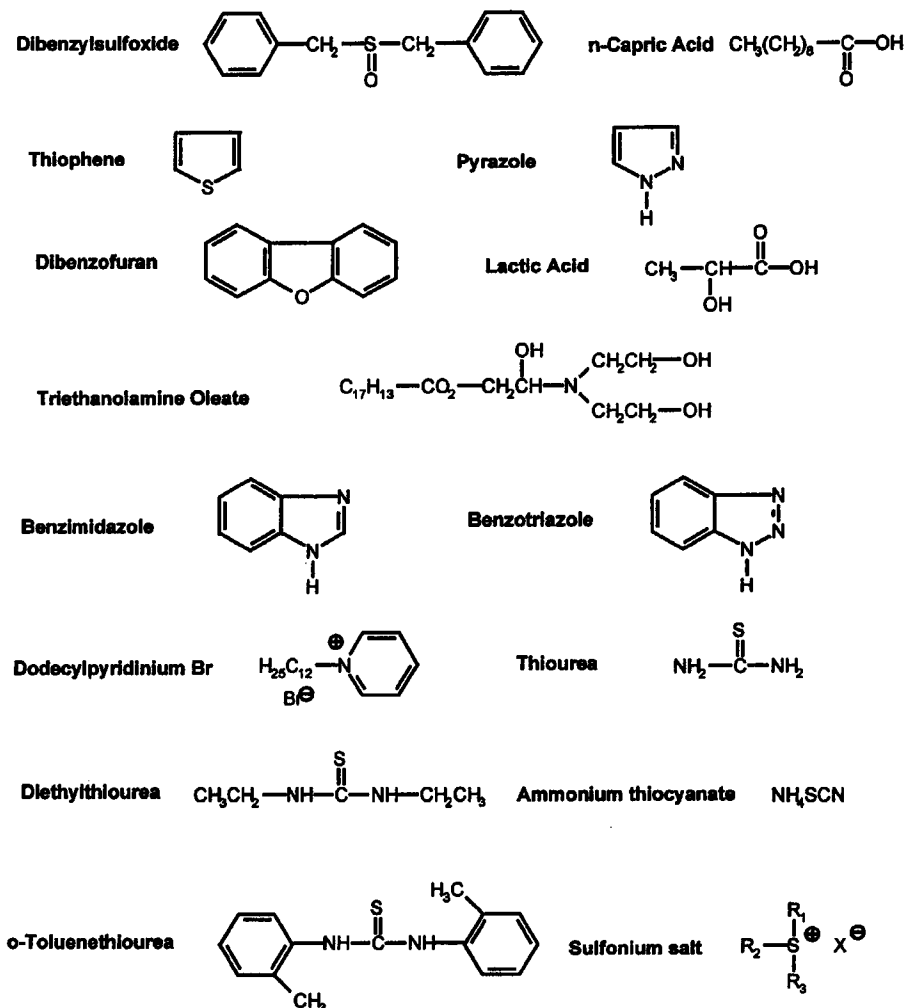


Figure 10. Inhibitors for HF, sulfuric acid, organic acids, and chelating agents.

containing 10% methanol (to keep the inhibitor dissolved).^{110,111} The inhibitors with the greatest electron density at the adsorption center ($>\text{C}=\text{S}$) performed best, e.g., benzaldehyde thiosemicarbazone.

Nonsulfur-containing compounds can also be effective inhibitors of ferrous metals in H_2SO_4 . Felloni et al.¹¹² studied a variety of compounds, including glyoxal, methyl alcohol, dioxane, dibenzyl sulfide, and benzylamine on iron. Campanella and DeAngelis¹¹³ examined picolinic, nicotinic, and isonicotinic acids. All of these proved to be fairly effective corrosion inhibitors. Kulig¹¹⁴ studied mild steel corrosion in 4.5% H_2SO_4 containing various mono- and di-carboxylic acids and found that mixtures of formic/lactic acid and acetic/lactic acid give the best protection. Olefinic, amino, and hydroxy carboxylic acids are more effective than the corresponding aliphatic acids. Zingales et al.¹¹⁵ found that dibenzofuran and several derivatives are fair corrosion inhibitors of iron in 4.5% H_2SO_4 at 77°F (25°C) and are somewhat less effective at 122°F (50°C).

Szauer and Brandt¹¹⁶ studied adsorption of amine oleates on iron in 4.5% H_2SO_4 . Their results suggest that amines with two active groups in the molecule may be able

to cross link and provide a more protective corrosion barrier than amines with only one active group. Shankar and Vasu¹¹⁷ investigated inhibition of mild steel corrosion with benzotriazole and observed Temkin adsorption behavior in 4–5% H₂SO₄ but Langmuir behavior in 9% H₂SO₄, implying that in both cases there was interference with the anodic process.

Proskurnya et al.¹¹⁸ prepared various iodomethylates and iodoethylates of vinyl-methylpyrazoles and found them to be highly effective inhibitors of iron corrosion in H₂SO₄, suppressing both the anodic and cathodic reactions.

Sherstobitova et al.¹¹⁹ studied the kinetics of the H₂ evolution reaction at iron in 4.5% H₂SO₄ containing *n*-butylamine, pyridine, antipyrine, and condensation products of antipyrine with two aldehydes. They found that these compounds inhibit the corrosion reaction throughout the range of surface coverage in conformance with an adsorption isotherm, although some accelerate the H₂ evolution reaction at low and intermediate coverage, which are not in conformance with the isotherm.

Zucchi et al.¹²⁰ tested a variety of alkynes and alkynols and found that 1-decyne was the best inhibitor, providing 99% protection to iron in 5% (1 N) to 20% H₂SO₄ with an inhibitor concentration of 10^{−4} M. In contrast, propargyl alcohol (1-propyn-3-ol) provides no protection whatsoever, but is reduced to allyl alcohol.¹²¹ It is well known that the addition of small amounts of halide ions, even Cl[−], can enhance the effectiveness of various inhibitors in H₂SO₄.^{122,123} Indeed, the halide ion itself acts as an inhibitor at low concentrations.¹¹⁰ The effect is particularly dramatic with some oxygen-containing inhibitors, such as acetylenic alcohols and unsaturated aldehydes. For example, cinnamaldehyde was able to provide little or no protection to mild steel in plain 15% H₂SO₄ at 65°C; however, when 1% Cl[−] was added, greater than 95% protection was realized.⁴³ The synergistic effect increases in the order Cl[−] < Br[−] < I[−]. The pseudo-halide SCN[−] also promotes the inhibition and, interestingly, so does HS[−] (from H₂S). Aromatic nitrogen salts exhibit a similar synergism. Frignani et al.¹²⁵ showed that *N*-decyl pyridinium halides display this behavior, evidently as a result of co-adsorption of the halide and the quaternary cation. Halides of other alkylpyridines, *p*-alkylbenzylpyridine, and *p*-alkylbenzyl quinoline are also very effective, especially in combination with KI.²⁶

Vasilyev¹²⁶ tested mixtures of acetylenic and nitrogen compounds and found a synergistic effect that increased with temperature. The addition of KCl further improved the inhibition, as did Sn²⁺ and Cr³⁺; the latter seemed to cause the films to be thicker. Synergism was also observed between amines and acids. For example, *n*-dodecylamine and *n*-capric acid give much higher protection to mild steel in 4.5% H₂SO₄ at room temperature than does either inhibitor alone.¹²⁷ Even castor seed and black pepper show synergistic effects, suppressing both the anodic and cathodic reactions.¹²⁸

For copper corrosion in hot H₂SO₄, Ross and Berry¹²⁹ found that benzotriazole (BTA) inhibits the rate of copper dissolution; flow rate and aeration change the inhibitor concentration profile, and a film composed of the cuprous salt of BTA is formed.¹³⁰ Other effective inhibitors for copper in H₂SO₄ include 2,4-dinitrophenylhydrazine,¹³¹ benzimidazole, indazole,¹³² and quinoline.¹³³ Various azoles appear to be effective corrosion inhibitors for brass, as well as copper.¹³⁴ Finally, Subramanyan et al.¹³⁵ studied the corrosion inhibition mechanisms of the alkaloids quinine (C₂₁H₂₂N₂O₂) and strychnine (C₂₁H₂₂N₂O₂). Both compounds inhibit the corrosion of copper, in 1% H₂SO₄ at 86°F (30°C), relatively well, and both chemisorb and

preferentially suppress the cathodic reaction, but increase the anodic Tafel slope. For general references on these subjects, see Reference 2 of Chapter 2.

The same types of compounds that are effective in HCl can usually inhibit phosphoric acid (H_3PO_4). A formulation of a large alkyl amine, e.g., dodecylamine, with KI is usually quite effective at low temperatures.¹³⁶ At higher temperatures, that is, up to 180°F (82°C), benzylquinolinium thiocyanate was found to be quite effective. Recently, Fouda et al.¹³⁷ studied some heterocyclic quaternary ammonium compounds (bicyclo nitrogen salts) and found they stimulated the cathodic reaction, although they substantially decreased the open circuit current density; thus, the inhibition is due solely to suppression of the anodic reaction.

Sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$), a dry solid, is usually mixed with water on site. It is effective for removing carbonate scales, but it must be mixed with NaCl to be effective in removing oxide scales.¹³⁸ Because it is relatively mild compared with the other mineral acids, $\text{NH}_2\text{SO}_3\text{H}$ is often used to clean mixed metal facilities. It cannot dissolve CaSO_4 or silicates, and it hydrolyzes at elevated temperatures to form insoluble sulfates. Thus, it is used primarily for small jobs, in which convenience in handling and transport are important. Generally, inhibitors that are effective in H_2SO_4 are also effective in $\text{NH}_2\text{SO}_3\text{H}$, but higher concentrations are usually required.⁶

Nitric acid (HNO_3) is used only in specific applications, primarily in descaling stainless steel. The HNO_3 can passivate the base metal, but it is dangerous because depassivation occurs at low concentrations. By the same token, however, it is very difficult to inhibit such a strong oxidizer. For example, HNO_3 oxidizes thiourea to dithioformamide, which hydrolyzes to diamino carbonyl disulfide.⁵⁹ However, it appears to be possible to inhibit moderately concentrated HNO_3 solutions (usually $\leq 15\%$) as well as mixed solvents containing HNO_3 , such as solutions of HNO_3 and HF or H_2SO_4 .

Sulfur-containing compounds such as mercaptans, sulfides, and thiols were the most widely used to inhibit corrosion of ferrous metals in HNO_3 . Recently, pyridine thiocyanate derivatives, particularly benzyl-2-methylpyridine thiocyanate,¹³⁸ were shown to be quite effective. Anoshchenko and Zorchenko¹³⁹ reported that a mixture of $\text{Al}_2(\text{SO}_4)_3$, KBr, and thiourea inhibited iron dissolution in an $\text{H}_2\text{SO}_4/\text{HNO}_3$ solution. Recently Srivastava and Srivastava¹⁴⁰ reported that even garlic is effective in HNO_3 at concentrations up to 22% (4 N) at temperatures ranging up to 174°F (79°C). Mixtures without sulfur-containing compounds also can be effective steel corrosion inhibitors. Stanford¹⁴¹ claimed that a formulation consisting of a Mannich reaction product (hydroabietylamine with formaldehyde and a larger aldehyde) and an acetylenic alcohol will inhibit steel corrosion in HNO_3 over a wide range of temperatures and acid concentrations.

Copper and brass can be effectively inhibited in dilute HNO_3 . Desai and Thanki¹⁴² found that anthranilic acid and *m*-aminobenzoic acid are effective inhibitors for 60/40 brass. Aminophenols can be effective on both copper and brass,¹⁴³ as can substituted anilines, *o*-anisidine, and *o*-phenetidine.¹⁴⁴ Heterocyclic amines are also good inhibitors.^{145, 146}

Sulfur/nitrogen compounds can also be effective inhibitors for copper and brass in dilute HNO_3 . Thiourea derivatives¹⁴⁷ and *p*-thiocresol¹⁴⁸ perform quite well. Shah and Trivedi¹⁴⁹ found that sodium diethyl dithiocarbamate is effective on brass, and Patel et al.¹⁵⁰ discovered the same for mercaptobenzothiazole (the Soviet inhibitor Captax) and various imidazoles, although benzimidazole (as opposed to its derivatives) is not very good at all.

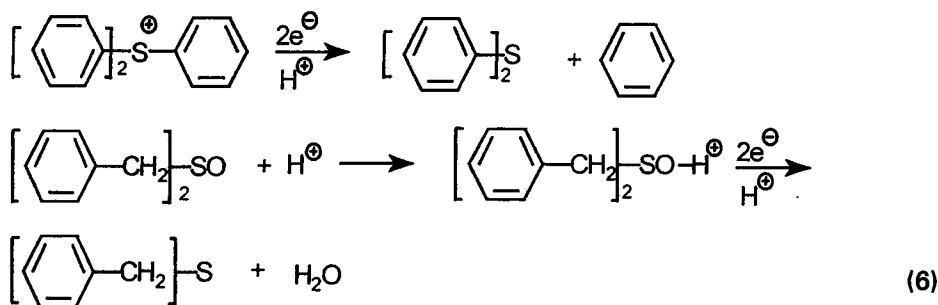
Although H_2SO_4 or H_3PO_4 can often be used in place of HCl to clean steels susceptible to stress corrosion cracking (such as the alloyed steels used in superheaters and preboiler systems), their high cost and tendency to form insoluble salts make them less than ideal chemical cleaning solvents. In addition, highly corroded boilers cleaned by mineral acids are susceptible to localized attack. Thus, the industry began a quest for more suitable cleaning agents, which led to the development of solvents based on organic acids and chelating agents.

The mechanisms by which many corrosion inhibitors function were elucidated over the past 50 years. The reader is referred to the treatise by Damaskin et al.¹⁵¹ for an excellent introduction to this subject.

Most neutral nitrogen compounds, such as benzotriazole or quinolinic, are thought to function by an acid/base reaction that involves sharing of the lone pair of electrons on the nitrogen with a metal ion or atom; the effect most often observed in potentiodynamic tests is suppression of the anodic reaction.¹¹⁷ In contrast, charged species, such as pyridinium or quinolinium salts, or readily protonated amines preferentially suppress the cathodic reaction.¹²⁵ The latter are thought to function by the formation of an ion pair with Cl^- on the surface, but acid/base interactions cannot be completely discounted. As discussed below, in strong acid even the neutral nitrogen compounds tend to become protonated; thus, the surface-inhibitor bonds of these species may take on more of an ionic character with increasing acid concentration.

Horner et al.¹⁵² have studied the mechanisms by which onium compounds inhibit steel corrosion. Kichigin et al.¹⁵³ studied tetra-*n*-butylammonium cation (TBA^+) and other quaternary nitrogen compounds in the presence of iodide, and Aramaki et al.¹⁵⁴ studied TBA^+ in the presence of halides, SO_4^{2-} , SCN^- , SH^- , NO_3^- , and N_3^- . In all these cases, halides were shown to be necessary for good inhibitor performance and the observed behavior was consistent with competitive co-adsorption of ion pairs (side by side). Sulfonium derivatives also require the presence of halide ions and, likewise, apparently co-adsorb to form ion pairs on the surface. As discussed below, unsaturated oxygen compounds, such as aldehydes and acetylenic alcohols, also require a halide ion for good performance.

Some inhibitors are reduced on the surface to yield secondary products that are themselves the active inhibitors. In strong mineral acids, elements from Groups VI and VII tend to become protonated, a necessary prerequisite for many reduction reactions. Such is the case for triphenyl benzyl phosphonium chloride,¹⁵⁵ which forms triphenyl phosphine, and triphenyl arsenic oxide, which undergoes protonation (permitting it to dissolve) and forms triphenyl arsine on the surface. Some sulfonium salts, e.g., tribenzylsulfonium hydrogen sulfate, and dibenzylsulfoxide also can be reduced by iron in HCl .



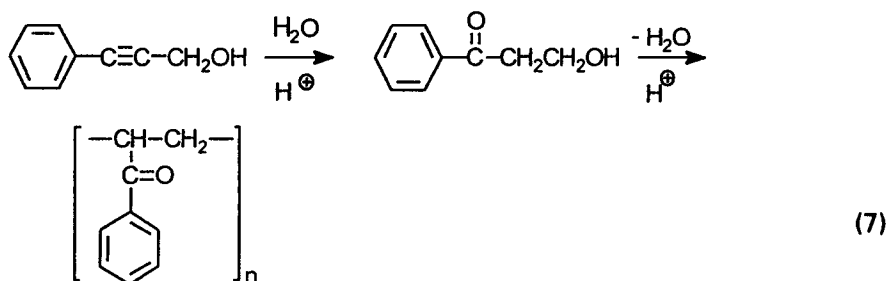
"Filming" amines, such as polymethylene imines and diamines, almost certainly undergo reduction on the surface; protonation may very well be involved as an initiating step. Quaternary nitrogen salts may also undergo reduction reactions, but there currently is no evidence to that effect.

Oxygen compounds can undergo protonation in mineral acids, a reaction critical to film formation. Aldehydes apparently protonate and appear to co-adsorb with SH^- , thus functioning in a synergistic manner.¹⁵⁶ Olbertz²⁴ studied a large number of aliphatic aldehydes and benzaldehyde derivatives with and without H_2S , and found a substantial synergistic effect in 16% HCl. To check for the formation of thioaldehydes on the surface, he tested a number of ketones and found no synergistic effect whatsoever, indicating that thioaldehydes are not formed in the former case, but rather that SH^- and the protonated aldehyde undergo ion pair formation on the surface. Cinnamaldehyde also appears to undergo protonation, either in solution or on the surface, and shows great improvement in inhibitor effectiveness when halide ions are present⁴³: in 19% H_2SO_4 (4.4 N), a surfactant/cinnamaldehyde mixture provides only 50% protection to mild steel (149°F [65°C]), whereas in 15% HCl (4.4 N) it can provide 98% protection.

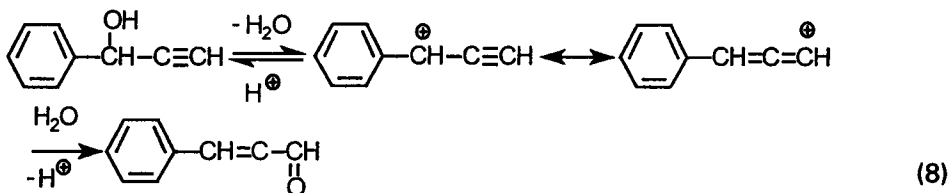
Acetylenic alcohols also appear to be protonated in strong mineral acids, either in solution or on the steel surface. It is now well established that acetylenic alcohols function primarily by chemisorption.^{17,23} Recent work by Growcock et al.¹⁵⁷ on 1-octyn-3-ol indicates that chemisorption involves donor/acceptor bonding of the protonated form of the inhibitor and that halide ions are necessary for good inhibitor performance. Furthermore, octynol undergoes reduction reactions on the surface to yield conjugated dienes and ultimately a film comprising low-molecular-weight hydrocarbon (2–5 monomer units long) with some double-bond unsaturation. Pathania and Poling's electrochemical and infrared reflectance experiments¹⁵⁸ showed that the chemisorbed layer of other acetylenic alcohols, which is only a few angstroms thick, reduces the Fe/Fe^{2+} exchange current density by 100-fold, and that growth of the polymer film results in significant additional reduction of the current. Using *in situ* ellipsometry, Jovancicevic et al.¹⁵⁹ confirmed that the chemisorption/film formation mechanism is operative even in relatively weak HCl (0.01 N); a chemisorption/film formation mechanism is also operative in H_2SO_4 , but the details differ from the HCl mechanism. Using AC impedance spectroscopy, Epelboin et al.¹⁶⁰ showed that 2-butyne-1,4-diol on iron in H_2SO_4 increases the charge transfer resistance with increasing exposure time. Later, Hausler¹⁶¹ showed that 2-butyne-1,4-diol can be just as effective in highly concentrated HCl (>20%) as it is at lower concentrations, e.g., 5%. The system is sensitive to O_2 but the effect is complex: over certain ranges of temperature and acid/inhibitor concentration, O_2 hinders the inhibition, while elsewhere it can substantially aid the inhibition.

On one hand, the aliphatic acetylenic alcohols are relatively stable in the acid itself (in protonated form) and undergo reaction only in the presence of an electroactive metal surface. On the other hand, aromatic acetylenic alcohols tend to react further with the acid, as well as with the metal surface, forming products which themselves are active inhibitors.^{45,46} These secondary products may function as intermediates and continue to react, either on the surface or in solution, to yield an adherent low-molecular-weight polymer film. For example, 3-phenyl-2-propyn-1-ol undergoes acid-catalyzed hydrolysis (protonation and hydration) in the solution to

form *p*-hydroxypropioiophenone (possibly protonated), which can dehydrate and polymerize on the steel surface to form poly(phenyl vinyl ketone).⁴⁶

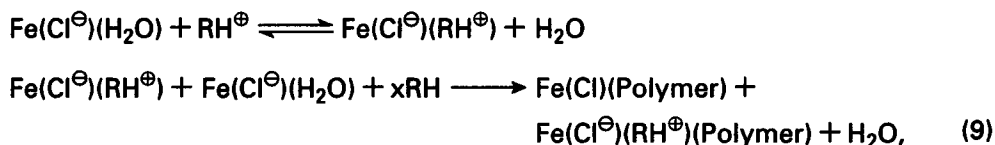


In contrast, 1-phenyl-2-propyn-1-ol undergoes protonation and dehydration, followed by hydration and deprotonation.⁴⁶



Both the allyl cation and cinnamaldehyde can adsorb on the steel surface, reacting further to yield various oligomers.

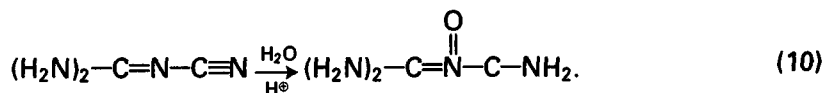
The film forming, oxygen-containing compounds examined to date all appear to undergo reversible chemisorption on steel in HCl, followed by polymerization reactions that form a barrier film over the entire surface. These general steps may be summarized with the following scheme¹⁵⁶:



where the braces denote adsorbed species and R is the inhibitor, which is assumed to be protonated (RH^+). Chemisorption involves displacement of water from the Cl-covered surface, followed by reductive condensation of the inhibitor on the surface with dissolved inhibitor. An envelope of polymer forms over active surface sites (first product), anchored at sites covered with monomer (second product).

Reactions of inhibitors with the acid are not always welcome. In fact at a sufficiently high temperature or high acid concentration, most inhibitors will undergo hydrolysis or chloride addition to the double bond that destroys their surface activity.¹⁶¹ Unsaturated oxygen compounds, such as acetylenic alcohols and unsaturated aldehydes, undergo acid-catalyzed polymerization reactions in solution if the acid concentration is above 20–30% or the temperature exceeds 199°F (93°C).³ Dicyandiamide

can undergo acid hydrolysis as follows:



Thus, for any application of an inhibitor, it is important to understand its environmental limitations.

Studies of thiourea and various derivatives suggest possible mechanisms for the dual nature of these compounds: at a low inhibitor concentrations they are corrosion inhibitors, and at high concentrations they act as corrosion accelerators. Pillai and Narayan⁶⁴ showed that indeed the mechanism in 4–12% HCl at room temperature changes in the concentration range of 4–40 μ M.

Some corrosion inhibitors have properties that are normally associated with surfactants. Recently, Pebere et al.¹⁶² studied 2-hexadecylimidazoline and 2-hexadecylimidazole as inhibitors of a carbon steel in HCl containing H_2S , and they obtained a protection vs. inhibitor concentration profile similar to that often seen with cationic surfactants; that is, there was a sharp increase in protection below the critical micelle concentration (CMC) followed by a leveling off at the CMC. Above the CMC, the inhibitors appear to form thick adherent films that act as diffusion barriers. In contrast, a study of the effects of ethoxylated alcohols (nonionic surfactants) and quaternary nitrogen salts (cationic surfactants) on the performance of the inhibitor cinnamaldehyde on mild steel in 15% HCl indicates that in these cases the surfactants co-adsorb with the inhibitor and produce a maximum effect far below their CMCs.⁴³

Mechanistic studies are beginning to shed some light on the synergistic effects observed between quaternary ammonium compounds and acetylenics/aldehydes, between nitrogen-containing compounds and sulfur-containing compounds, and between sulfur compounds and acetylenics/aldehydes. In all these cases, the mechanisms appear to involve co-adsorption. In the cases involving sulfur compounds, we speculate that they form a structure on the surface akin to SH^- , thus providing a negatively charged surface on which cationic quaternary nitrogen compounds (nitrogen salts) or protonated acetylenics/aldehydes can form ion pairs. In a manner analogous to the halide/nitrogen salt synergism described above, the sulfur compound and protonated oxygen or nitrogen compound competitively co-adsorb. In the cases involving quaternary nitrogen compounds and protonated acetylenics/aldehydes, both adsorbing species are cationic, and the adsorption may well be dominated by attractive interactions among the chains of the adsorbed species.

Structure activity studies have not revealed many surprises. Chakrabarti¹⁶³ studied four cyanoguanidine (guanidine, $NH_2-C \equiv NH$) derivatives to determine the effect of electron density distribution on inhibitor performance for mild steel in 6% HCl. Using Huckel molecular orbital calculations, he determined that the inhibition directly correlated with the ionization potential (IP) and inversely with the electron affinity (EA). Thus biguanidine monohydrochloride, at a concentration of 0.02 M, gave the highest protection (95.5% in a 1-h test), and had the highest IP and the lowest EA. Szklarska-Smialowska and Wieczorek¹⁶⁴ determined that the performance of an inhibitor that acts solely by covering surface sites is a function of its solubility, the presence of functional groups, and interaction among the adsorbed molecules.

Linear free-energy relationships for correlating molecular structure to inhibiting ability are still popular. One such relationship,

$$\log(I_x/I_j) = a\Sigma\sigma + bE_s + C + d, \quad (11)$$

describes the relative effectiveness of an inhibitor I_i to that of its parent molecule, I_j , as a function of dipolar contributions, a , steric effects, E_s , and electron delocalization, C .¹⁶⁵ Here a , b , and d are constants. The general trend found in the past for the effect of an alkyl chain length appears to be almost universal: optimum inhibitor efficiency for relatively polar parent molecules results with a carbon chain length usually in the range of C₈–C₁₂. This effect is attributable to the opposing effects of reduced solubility and increased adsorbate interaction with increasing chain length. Some substituents provide a second site with high electron density (a Lewis base site), such as an atom with a nonbonded pair of electrons. Still other substituents, such as alkyl groups, can produce inductive effects, while others may lead to stabilization or destabilization of reaction intermediates or products, e.g., resonance stabilization of aromatic compounds or their reaction products. In a study of nitrobenzene derivatives on pure iron in 20% HCl,⁸⁰ it was first learned that these compounds generally accelerate the cathodic reaction (a result of reducing the inhibitor to a hydroxylamine and ultimately an amine) but inhibit the anodic reaction. Inhibitor effectiveness increases along with the electron-withdrawing ability of the substituent, which is closely related to the back-donation of metal electrons to antibonding π orbitals. Thus, olefinic amines and anilines, which possess such orbitals, are much better than alkyl amines, which do not.

Inhibitors for Organic Acids and Chelating Agents

Chemical cleaning solvents containing organic acids, chelating agents, and mixtures of these chemicals captured a large portion of the chemical cleaning market during the past 20 years. These solvents can be inhibited and used to clean sensitive alloys, such as austenitic and ferritic stainless steels, and will not cause stress cracking of these alloys. In addition, they generally are less toxic and can be used at higher temperatures than the mineral acids. The chemical structures of several classes of inhibitors used in these solvents are shown in Figure 10.

Citric acid and acidic ammonium citrate solutions were used to remove iron oxide and copper from utility power boilers.¹⁶⁶ Several recent publications described the corrosion and inhibition properties of citric acid solutions. Blume¹⁶⁷ compared the corrosion rates of citric acid, ammonium citrate, mixtures of hydroxyacetic acid/formic acid and hydroxyacetic acid/citric acid for carbon steel, and stainless steels (304 and 430). The corrosion rates of the carbon steels were moderate (0.05–0.1 g/cm²/day), and were reduced by about 50% by a commercial inhibitor. Organic solvents gave about the same rates, and the stainless steels were essentially uncorroded. However, neither the test conditions nor the nature of the inhibitor was revealed. Arrington et al.¹⁶⁸ tested several boiler metals in ammoniated citric acid (pH of 6.0) at 257–275°F (125–135°C). A proprietary inhibitor limited the corrosion rate of A213 T11 steel to 0.008 g/cm²/day and 1020 carbon steel to 0.002 g/cm²/day. A study by Bradley¹⁶⁹ demonstrates one of the major problems encountered with the use of organic inhibitors in cleaning solvents. Ammonium citrate (pH of 3.5) was used to dissolve magnetite (Fe₃O₄) from steel boiler tubes, followed by a high (9.5–10) pH copper dissolution stage using ammonium bromate or sodium nitrite. Three commercial inhibitors

(unidentified) interfered with the removal of copper, especially when air/ NaNO_2 was the oxidant.

Petit and McTigue¹⁷⁰ tested several organic acid mixtures with carbon and alloy steels as part of a program to develop solvents, which would remove magnetite and "sludge" from pressurized water (PWR) nuclear reactors. The solvents tested were ammonium citrate, citrate/EDTA (ethylenediaminetetraacetic acid), ammonium HEDTA (hydroxyethylethyl-enediaminetriacetic acid), citric/HEDTA, and citric/ascorbic acid. Diethylthiourea (DETU) or a proprietary inhibitor was used. The DETU was adequate at 185°F (85°C), for most of the solvents, but the proprietary inhibitor was required at 257°F (125°C). In some cases, the A516 carbon steel was pitted by solutions inhibited by DETU.

A general chemical cleaning inhibitor was described by Kennedy.¹⁷¹ This formulation consists of an alkylpyridinium or quinolinium salt, such as dodecylpyridinium bromide (DDPB) and a sulfur compound such as thiourea (TU) or ammonium thiocyanate. The author claims that this mixture will protect a variety of carbon and alloy steels in solvent that include HEDTA, ammonium EDTA (pH of 5 and 9), EDTA/citric acid, EDTA/formic acid, and hydroxyacetic/formic acid mixtures. The temperatures range from 203°F to 302°F (95–150°C). Proprietary inhibitors containing nitrogen and sulfur compounds also are reported to protect carbon and alloy steels from attack by HEDTA acid (pH of <3) solutions.¹⁷² The solvents were tested at 149°F and 203°F (65°C and 95°C), and corrosion rates were below 0.005 g/cm²/day for 1018 CS, SA209T1A, and SA213T22 alloy steels.

The EDTA is a major component in many chemical cleaning solvents. This chemical will dissolve and complex iron over a wide range of acidity (pH of 4.5–10.0), and can be used with other additives (organic acids and reducing agents such as hydrazine) for specialized cleaning purposes. Removal of copper deposits can be accomplished by adding an oxidant to the alkaline solution of iron EDTA.¹⁷³ The ammonium salts of EDTA as well as HEDTA, NTA (nitrilotriacetic acid), DTPA (diethylenetriaminepentaacetic acid), and citric acid were tested at 325°F (163°C) with 1010 carbon steel.¹⁷⁴ The pH was 9.2, and 0.1% of a commercial inhibitor containing nitrogen and sulfur compounds was used. In all cases, the corrosion rate was <0.005 g/cm²/day. These solutions were used to dissolve magnetite from utility power boiler tubes.

Brunet and Turluer¹⁷⁵ made an extensive evaluation of corrosion and inhibition in EDTA solutions containing citric acid and/or hydrazine. Inhibitors tested include benzotriazole (BZT), benzimidazole (BZI), BZI with gelatin, and a commercial inhibitor. All of these inhibitors reduce the corrosion of several types of steels. When the steel is coupled to magnetite, the potential is shifted in the anodic direction. With a large enough ratio between magnetite and bare steel, most of the inhibitors desorb. Only the commercial inhibitor was effective at a pH of 9 in the presence of magnetite.

Mixtures of EDTA with hydrazine (frequently also containing citric acid) received extensive evaluation as solvents for deposits found in nuclear steam generators. Pitzer¹⁷⁶ made the first solvents containing EDTA and hydrazine but did not conduct corrosion tests. Pocock and Leedy¹⁷⁷ tested a number of potential steam-generator cleaners at 149°F and 203°F (65°C and 95°C). An EDTA/citric acid hydrazine mixture was compared with thioglycolic acid, hydroxyacetic/formic, citric/formic, and citric/formic-hydrazine. All of the solvents were inhibited with commercial inhibitors. The EDTA

formulation produced the lowest corrosion rate on carbon steel in both static and dynamic tests. There was a substantial difference between the EDTA/citric/ hydrazine solvents at a pH of 5 and 7. The rates on carbon steel were a factor of 4 higher at a pH of 5 as compared with a pH of 7.

Roberge and Gilbert¹⁷⁸ also investigated an EDTA/citric/hydrazine solvent in the presence of 1010 carbon steel at 203°F (95°C). A number of pure compounds were compared with a polymerized tetra imidazoline (called TIA here) and two commercial inhibitors containing diethylthiourea (DETU). The major goal of the study was to look at the effect of magnetite addition, as well as to try to develop an inhibitor system that does not contain sulfur. In the absence of magnetite, the commercial inhibitor gave the best protection, followed by hexynol. A similar acetylenic alcohol (ethyloctynol) was an accelerator. The addition of magnetite had a large effect on the corrosion protection provided by the inhibitors. In addition, the source of the magnetite was important. The diethylthiourea inhibitors (pure and formulated as commercial inhibitors) provide excellent protection in the presence of magnetite from Fisher Chemical, but little protection in the presence of magnetite from Anachemic. Overall, a mixture of benzotriazole with two nonionic surfactants provided the lowest corrosion rates in the presence of the various magnetites (although not the lowest percentage of protection, because the base rate depended on the magnetite source). The mechanism of inhibition in the presence of inhibitors, magnetite, and hydrazine is quite complex, and it seems to involve the rate at which the magnetite dissolves, and the concentration of residual hydrazine. Hausler¹⁷⁹ investigated the EDTA/citric/hydrazine system containing TIA. He also found a complex corrosion behavior in the presence and absence of magnetite and hydrazine. He attributes the complex nature of this system to the formation of chelate complexes in the interphase between the solution and the metal's surface.

Hausler¹⁸⁰ tested 150 compounds in a solution of 10% EDTA, 1% N₂H₄, and a pH of 7.0 with NH₃. The solution also contained 17.5 g/L Fe₃O₄ (to simulate dissolving scale). Only sulfur-containing compounds, such as dibutylthiourea, TIA, and alkylpyridines gave more than 90% protection in the initial screen. The sulfur compounds and the alkylpyridines were rejected because of solubility problems. A new class of compounds (imino-amido condensation products) containing thioether linkages was synthesized, and it was found to give >90% protection at 154°F and 257°F (68°C and 125°C). A final experimental formulation was made. The TIA was rejected because it would not protect SA-533-A steel at 257°F (125°C). The experimental formulation was then used in a pilot size ("pot boiler" and model boiler) with EDTA/hydrazine to clean sludge and remove magnetite from simulated crevices.¹⁸¹ Some concern was expressed about the sulfur content (~1.25%) in Hausler's experimental formulation, because there are fears that residual sulfur may cause cracking of the Alloy 600 tubes found in nuclear steam generators. This subject was examined extensively by EPRI and was found to not be of concern.¹⁸²

The most successful inhibitor formulations for organic acids and chelating agents contain amines, reduced sulfur compounds, or combinations of a nitrogen compound (amine, quat, or polyfunctional compound) and a sulfur compound. The only major exceptions are the sulfonium compounds. Jofa¹⁸³ investigated the mechanism of mixtures of quaternary ammonium or alkyl ammonium compounds used with sulfur compounds, such as thiourea. He concluded that the sulfur compounds form HS⁻ ions

in solution. These adsorb onto the iron surface, thus attracting the cationic amine inhibitor.



I believe that the nitrogen/sulfur inhibitors function in a similar manner in the chemical cleaning solvents. The sulfur-containing inhibitors must be used with some of the special alloys found in nuclear steam generators. Currently, there is no complete explanation for the specificity of these metals for the nitrogen/sulfur combination.

An examination of the references described reveals that hydrochloric acid solvents require quaternary nitrogen or amine-based formulations plus an unsaturated oxygen compound. All of the other cleaning formulations requires a nitrogen compound plus a sulfur-containing molecule. Virtually all commercial chemical cleaning inhibitor formulations contain these active ingredients.

Special Problems

Boilers and nuclear steam generators frequently are tubed with alloys that have small amounts of Cr and Mo. Austenitic and ferritic stainless steels (Series 300 and 400 steels) also are encountered in addition to carbon steels. The inhibitors are usually developed by using the less expensive carbon steels; these inhibitors will not protect the Cr steels, or higher concentrations of inhibitors may be required. Frenier and Loescher¹⁸⁴ studied the corrosion of six different power boiler metals in ammonium EDTA (pH of 9.2) at 325°F (163°C), HCl at 160°F (71°C), and HCl with thiourea (a copper complexer) at 160°F (71°C; see Tables 4–6). All three solvents were inhibited with commercial inhibitors that contained nitrogen and sulfur compounds. For the EDTA and HCl/thiourea solvents, the Cr/Mo steels required more inhibitor, or experienced higher corrosion than the low carbon steels (SA210 and SA178C). In HCl without thiourea, there was no significant difference between the steels. Frenier and Loescher¹⁸⁴ also determined corrosion rates, and they performed metallurgical examinations of welded carbon steels. Only a poor quality “stick” (arc) weld experienced any perceptible preferential attack. The high-quality tungsten inert gas (TIG) and metal inert gas (MIG) arc welds did not experience significant preferential attack.

Preferential attack on special metals, i.e., Alloy 600, and stressed and welded carbon steels (SA210 GR-C and SA508-CL-II), was of special concern to the developers of the steam-generator cleaning solvent containing EDTA, hydrazine, and a sulfur/nitrogen inhibitor.¹⁸⁵ There were significant differences in the response of various carbon steel alloys in the EDTA/hydrazine solvent. The A-533-B ring material experienced the most corrosion of the metals tested, and it was very sensitive to the amount of hydrazine present. The corrosion always increased with the increasing concentration of hydrazine. These solvents always contained magnetite to simulate the dissolution of scale. We also note that Hausler¹⁸⁰ had to modify the cleaning inhibitor because of the high corrosion rates experienced by SA-533-A steel.

Poulson and Robinson¹⁸⁶ assessed the possibility of stress corrosion cracking for mild steel in inhibited HCl and mild steel and 9Cr-1Mo steel in inhibited ammonium

TABLE 4

Static Corrosion Rates (lb/ft²/day)^(A) in 4.5% Ammonium EDTA (pH of 9.2) at 325°F (163°C); Inhibitor "A" Used

Metal	0.1% A	0.15% A	0.2% A	0.3% A	0.4% A
A. $s/v = 0.6 \text{ cm}^{-1}$					
SA213T11	0.094	0.082	0.033	0.027	
SA209T1a	0.084	0.064	0.037	0.015	
SA178C	0.070	0.040	0.023	0.012	
SA210C	0.068	0.063	0.036	0.016	
B. $s/v = 0.8 \text{ cm}^{-1}$					
SA213T11			0.060	0.030	0.019
SA209T1a			0.062	0.017	
SA178C			0.026	0.017	
SA210C				0.013	
C. $s/v = 1.5 \text{ cm}^{-1}$					
SA213T11				0.028	0.017
SA209T1a				0.012	0.011

^(A)5 kg/m²/day.

citrate (commercial proprietary inhibitors were used). A sensitized 316 SS also was tested in inhibited ammonium citrate. The SCC tests were performed using "C" rings deformed above the yield stress, and slow-strain-rate tests also were performed. Mild steel did not crack in either HCl or citric acid. Cracking could be induced in the 9Cr-1 Mo using very harsh conditions, but not under actual use conditions (only if improperly heat treated). The 316 cracked only in boiling citric acid.

Ferric Ion Corrosion

Any time iron oxides are dissolved, iron ions are released into the cleaning solution. In most industrial equipment, the majority of the iron is found partially or totally in the 3+ oxidation state. When dissolved by the solvent, the ferric ions will reduce

TABLE 5

Static Corrosion Rates (lb/ft²/day)^(A) in 5% HCl With 1% Thiourea at 160°F (71°C); 0.1% Inhibitor "C" Used

Metal	$s/v = 0.3 \text{ cm}^{-1}$	$s/v = 0.7 \text{ cm}^{-1}$
SA213T22	0.016	0.039
SA213T11	0.020	0.047
SA210C	0.008	0.024
1018CS	—	0.015

^(A)5 kg/m²/day.

TABLE 6

Static Corrosion Rates (lb/ft²/day)^(A) in 10% HCl
at 160°F (71°C); 0.2% Inhibitor "C" Used

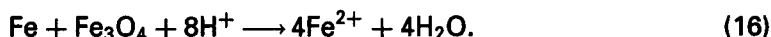
Metal	s/v = 0.3 cm ⁻¹	s/v = 0.7 cm ⁻¹
SA213T22	0.0063	0.0091
SA213T11	0.0090	0.016
SA210C	0.0023	0.016
1018CS	—	0.0064

^(A) 5 kg/m²/day.

when in contact with the bare metal surfaces as they are exposed by the cleaning solutions.



If the scale is quite thin, or is very electrically conducting, such as magnetite, a "reductive dissolution" process may take place and the iron ions may come into solution directly as ferrous ions.



If the scale is thick, or is predominantly ferric oxide (red rust or one of the hydrated iron oxides), a portion of free ferric ions will be released into the cleaning solvent and may cause corrosion damage at diverse places in the unit being cleaned.

Three methods have been devised to reduce the additional corrosion caused by the ferric ions in the scale being dissolved: (1) special ferric ion inhibitors, (2) reducing agents, and (3) complexers.

Most organic corrosion inhibitors used in cleaning solutions will not prevent ferric ion corrosion. Special chemicals were developed to reduce this problem. Alfandry¹⁸⁷ demonstrated that hexamethylenetetramine will protect steel in HCl, but the protection is reduced by the presence of Fe³⁺ ions. However, the protection provided to steel in sulfuric acid is improved by the addition of ferric ions to a solution inhibited by phenylthiourea. Streicher¹⁸⁸ reported that ferric ion corrosion of steel in sulfuric acid can be reduced by a mixture of diorthotolythiourea and an anionic surfactant, such as an alkyl-aryl sodium sulfonate. Sulfonium salts also were used as ferric ion inhibitors.¹⁸⁹⁻¹⁹² These inhibitors are effective in a variety of mineral and organic acids, but they are most effective in acidic (pH of 5) EDTA solutions. The sulfonium salts were shown to electroreduce at the corrosion potential to form a hydrophobic product (hydrocarbon) that may enhance the protection of the steel from oxidation by the ferric ion.



While ferric ion inhibitors are important in many cleaning processes, they are essential to clean open cooling water systems. If the cooling tower in such systems

cannot be bypassed, ferric ions would be continually regenerated during every pass of the cleaning solvent over the tower (which is a very efficient aerator).



Reducing agents (described below) would not be effective in such a highly oxygenated system. These agents are probably the “inhibitors” of choice during the cleaning of closed systems. Hydrazine was added to EDTA solutions to speed the dissolution of magnetite that was not in close electrical contact with steel. The nuclear steam-generator cleaning solutions described above are examples of the use of a reducing agent. In these cases, the hydrazine speeds the dissolution of the scale through a “reductive dissolution” mechanism, and it also reduces ferric ion corrosion. Shigehiro and Ueki¹⁹³ claimed the use of erythorbic acid (an isomer of ascorbic acid) with another organic inhibitor (not described) as a system for protecting steel from ferric attack in HCl and citric acid. This reducing agent can also speed the dissolution of iron oxide. Figure 11 shows the rate of dissolution of iron oxide with and without the reducing agent. The erythorbic acid was found to be more effective than other reducing agents, such as stannous chloride or hydrazine.

A proprietary reducing agent was described by Lawson et al.¹⁹⁴ This reducing agent was tested and found to be effective in HCl and hydroxyacetic/formic acid as well as in sulfamic acid solutions. Commercial organic inhibitors also were used in the cleaning solutions. Hydrogen sulfide (H₂S) also will reduce ferric ions in acidic solutions. Engel and Keeney¹⁹⁵ claimed that the use of a material capable of generating H₂S, such as thioacetamide or iron sulfide, will reduce the corrosion caused by HCl containing ferric ions. An aldehyde-containing organic corrosion inhibitor was also present to control the corrosion caused by the H₂S. Walker¹⁹⁶ described the use of hydroxylamine and copper as reducing agents in oilwell acid. Additional reducing agents that have been proposed for use in HCl to control ferric corrosion (or other

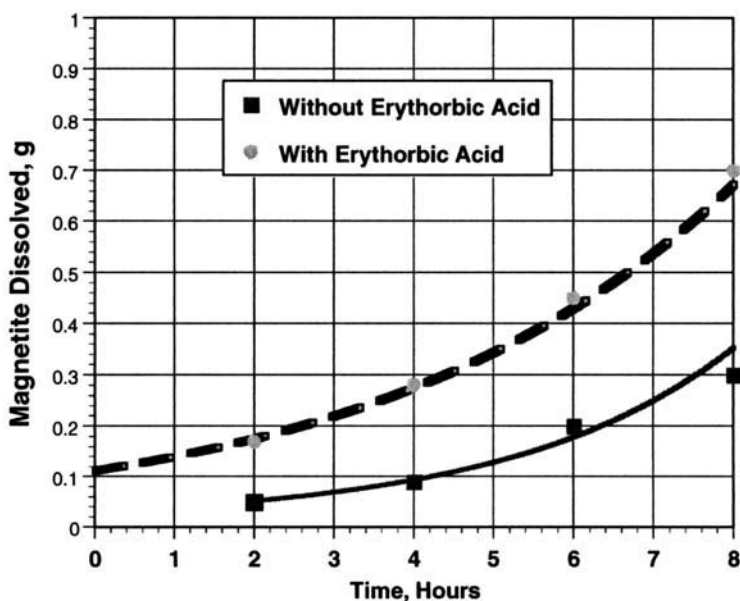
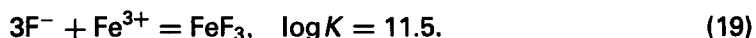


Figure 11. Effect of reducing agent on dissolution of iron oxide in HCl (dissolution of magnetite in 5% HCl at 150°F).

problems with ferric iron) include sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) with a copper catalyst¹⁹⁷ (also a KI catalyst) and diethylhydroxylamine (DEHA, $[\text{C}_2\text{H}_5]_2\text{-N-OH}$)¹⁹⁸, with or without a copper catalyst. The effectiveness of the reducing agents depends on the number of electrons available per molecule. Stannous chloride provides 2, sulfide 2, and hydrazine 4, but erythroic acid may provide as many as 8 (depending on the pH).¹⁹⁹

Fluoride ions have been reported to complex ferric in acidic solutions to such an extent that ferric corrosion is reduced or eliminated; see Equation (19).²⁰⁰



Bradley and Smith⁹⁷ reported that corrosion rates of exposed steel were much lower when mixtures of HF and HCl were used to dissolve magnetite, as compared to HCl. In both cases, an organic acid inhibitor was used to control the attack of the acid on the steel. Lower corrosion rates also were reported for HF solutions compared with similar concentrations of HCl. Similar results were noted by Alfandry.¹⁸⁷ Many of the complexers and reducing agents used in chemical cleaning also were used in oilfield acidizing fluids to control the precipitation of ferric hydroxide as the acid dissolves and spends on carbonate-containing formations (see Crowe¹⁹⁹).

Toxicity Issues

Many commercial acid inhibitors used in chemical cleaning services were based on the Mannich condensation reactions introduced by Saukaitis and Gardner,²⁰¹ Gardner and Saukaitis,²⁰² Mansfield et al.,²⁰³ and Monroe et al.²⁰⁴ This process uses formaldehyde, an amine, and a ketone to produce a Mannich base. Because this reaction rarely goes to completion, some formaldehyde will remain in the reaction product that is formulated as the commercial inhibitor. Formaldehyde was shown to be an animal carcinogen and appears on the OSHA Specifically Regulated Substance List and the National Toxicity Program Source List 9C (compilation of carcinogens); therefore, it is desirable to remove this substance from inhibitor formulations.

In addition to a condensation reaction product, commercial acid inhibitor formulations frequently contain acetylenic alcohols²⁰⁵ such as propargyl alcohol, hexynol, or ethyloctynol (see Figure 12 for chemical structures). While these materials can produce excellent corrosion inhibitor packages, many acetylenic alcohols are quite toxic to mammals (Table 7; Sax²⁰⁶) and the lower alcohols (propargyl alcohol and hexynol) are readily absorbed through the skin. For these reasons, there is a growing necessity to produce corrosion inhibitors that are less toxic than current formulations. In the late 1990s this started to occur.

Frenier and Growcock²⁰⁷ described formulations of α , β -unsaturated aldehydes with surfactants that were shown to be effective corrosion inhibitors for steel in HCl. Based on this technology, the aromatic compound *t*-cinnamaldehyde was proposed as an ingredient in low-toxicity inhibitor formulations.²⁰⁸ According to Growcock and Frenier³⁹ and Growcock,²⁰⁹ this aldehyde adsorbs onto the surface of the steel and then forms a low-molecular-weight polymer film that enhances the corrosion protection. A low-toxicity commercial inhibitor²¹⁰ formulation based on cinnamaldehyde was developed for use in HCl-base cleaning formulations. It is suitable for use in industrial cleaning solvents containing HCl or HCl containing ammonium bifluoride

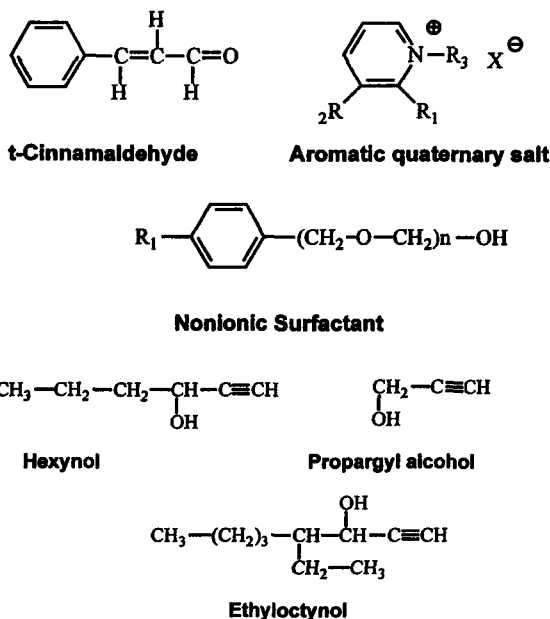


Figure 12. Additional inhibitors.

(ABF). Aquatic toxicity values are shown in Table 7. The inhibitor protects a variety of steel alloys as well as or better than currently used commercial acid inhibitors.

In Table 8 a comparison is shown of static corrosion rates for the low-toxicity inhibitor (B) compared with a classic Mannich-base inhibitor (A) that contains formaldehyde and hexynol. In most of the tests, the low-toxicity inhibitor provided similar or superior inhibition compared to the classic acid inhibitor. Inhibitor B also was used to clean a 600-ft (182.88-m)length of carbon steel piping that had a light coating of iron oxide and was cleaned in a chemical plant using the “yo-yo” method (see Figure 13). A solution of 7.5% HCl inhibited with 0.1% of inhibitor B was heated to 140°F (60°C), then pumped back and forth between two truck tanks. The iron and acid-strength curves during the cleaning are shown in Figure 14. The acid and iron concentrations reached stable values after 3 h of contact. The leveling trend observed for acid concentration and iron concentration confirms that the inhibitor was providing adequate protection to the piping being cleaned. After the acid had been flushed from the line,

TABLE 7

Mammal Toxicity Studies: Oral LD₅₀ Values for Rats

Compound	LD ₅₀ , mg/kg	Source
Propargyl alcohol	55	Sax Handbook ²⁰⁶
Hexynol	34	Sax Handbook
Cinnamaldehyde	2200	Sax Handbook
Formaldehyde	800	Sax Handbook
Dodecylpyridinium Br	320	Dow Chemical Co.
Naphthylmethylquinolinium Cl	644	Dowell Schlumberger, Inc.
Nonylphenol-ethylene oxide surfactants	1310	Sax Handbook

TABLE 8

Corrosion Rates (lb/ft²/day)^(A) Without Additives at 151°F
(66°C) and with 0.1% Inhibitor

Metal	[HCl], %	Inh. A	Inh. B
C1010	5.0		0.0014
C1010	7.5	0.0010	0.0011
C1018	5.0	0.0013	0.0007
A-515-Gr70	5.0		0.0014
A-515-Gr70	7.5	0.0045	0.0015
A-213-T22	5.0		0.0011
A-213-T22	7.5	0.0018	0.0021
A-213-T11	5.0		0.0019
A-213-T11	7.5	0.0013	0.0012
A-106	5.0		0.0015
A-106	7.5		0.0019

^(A)5 kg/m²/day.

a soda ash/sodium nitrite passivation stage was used to prepare the piping for use by the client.

A low-toxicity acid inhibitor was proposed by Johnston.²¹¹ This composition contains low-toxicity amines or quaternary nitrogen salts (abietyl amine or pyridine-containing rings), a divalent sulfur compound (such as ammonium thiocyanate), or a dialkyl thiourea derivative. Enhancer salts such as potassium iodide and solvents (propylene glycol) also may be present. High levels of inhibition in HCl solutions are claimed. Low-toxicity amides of fatty acids were described by Jiricek et al.²¹² When tested in 5% HCl at 113°F (45°C), very few of the amides provided >80% protection for carbon steel. Inhibitors for use in cleaning water wells were proposed by Anderson and Seigle.²¹³ The HCl (up to 15%) solution's attack on steel was inhibited by using a partially hydrolyzed protein such as gelatin or casein. The useful temperature range is from about 32°F (0°C) to about 90°F (32°C). A low-toxicity composition for use in HCl was patented by Carandang.²¹⁴ This complex mixture contains gelatin, a sugar-derived polymer such as sorbitol, and an iodide compound such as KI. Phosphoric acid, sodium sulfate, and propylene glycol also may be present. Frenier²¹⁵

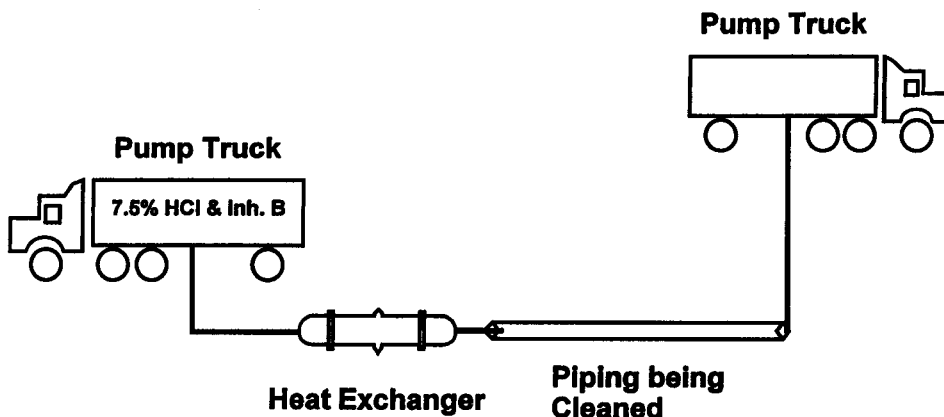


Figure 13. Yo-yo cleaning method.

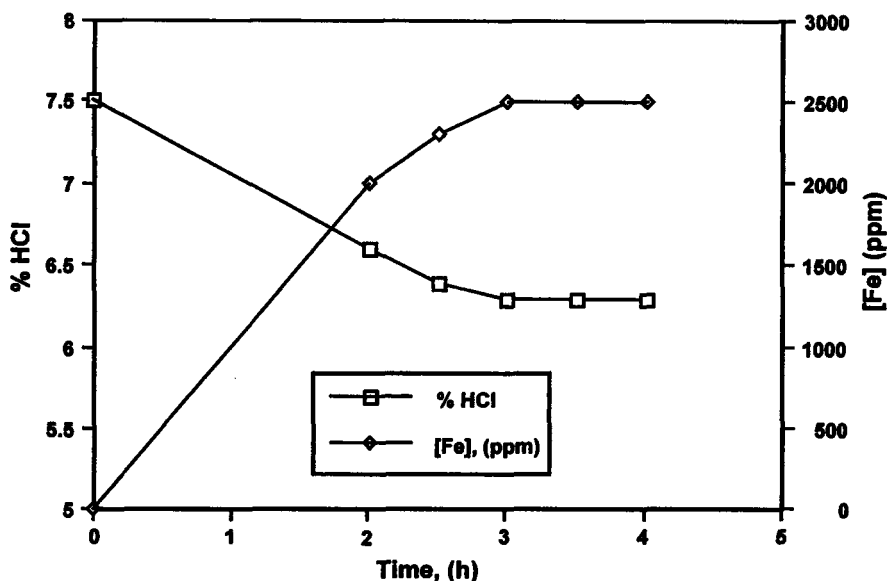


Figure 14. Dissolution of iron oxide from piping in a chemical plant at 140°F (60°C); HCl is inhibited with 0.1% inhibitor B.

reviewed several low-toxicity formulations based on quats and a unique propylene glycol-based reaction solvent for the aromatic quats.

CONCLUSIONS

Toxicity issues will continue to be some of the most important aspects of corrosion inhibitor technology, and meeting the demands for less toxic inhibitors will consume a large portion of the funds available to develop new formulations. Other issues such as flash point and presence of heavy metals will limit the palette available to the inhibitor formulator. A comprehensive review of “green” inhibitor technology was presented at the 2000 Ferrara, Italy inhibitor conference.²¹⁶

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5

SOLVENTS FOR REMOVING ORGANIC/MIXED DEPOSITS

The cleaning of refinery, petrochemical, and chemical plant process equipment is much different than the cleaning operations in power-generating plants, because of the presence of complex organic deposits as well as mixed organic/inorganic deposits. This chapter reviews procedures that have been used over the past 30 years for the removal of organic foulants, and the dissolution of iron sulfide deposits; new innovations for the removal of organic deposits are also reviewed.

CLASSICAL METHODS FOR CLEANING REFINERY UNITS

Refineries are primarily designed to change crude oil into its components. The major operations achieve separation of the various fractions, which together make up crude oil. This separation is accomplished by using pressures from partial vacuums to many hundreds of pounds. The chemical compositions and structures also may be changed. These reactions include alkylation and cracking processes that maximize the production of gasoline and more useful products. Chemical and petrochemical plants share many of the same types of units as refineries, and many of the deposits are similar to those found in refineries.

Notice the layout of a typical refinery (Figure 1).¹ Of course, this is extremely simplified, but it will serve to show the complexity of a modern refinery. This chapter goes through the major units with a description of the system, typical metals of construction, and problem areas that may require chemical cleaning. Please remember that all refineries are not alike; they will actually vary quite substantially. A very broad overview of these types of units and some of the fouling deposits that may be found in them is presented.

When the crude oil arrives at the refinery, either by pipeline or barge, it will be placed into a storage tank where some of the solids will settle out. While in the tank, the crude will be tested for various items, such as American Petroleum Institute (API) gravity, water content, and metal and mineral content, and to determine the compositions of its oil fractions. This testing will help to determine the parameters required to process the crude oil.

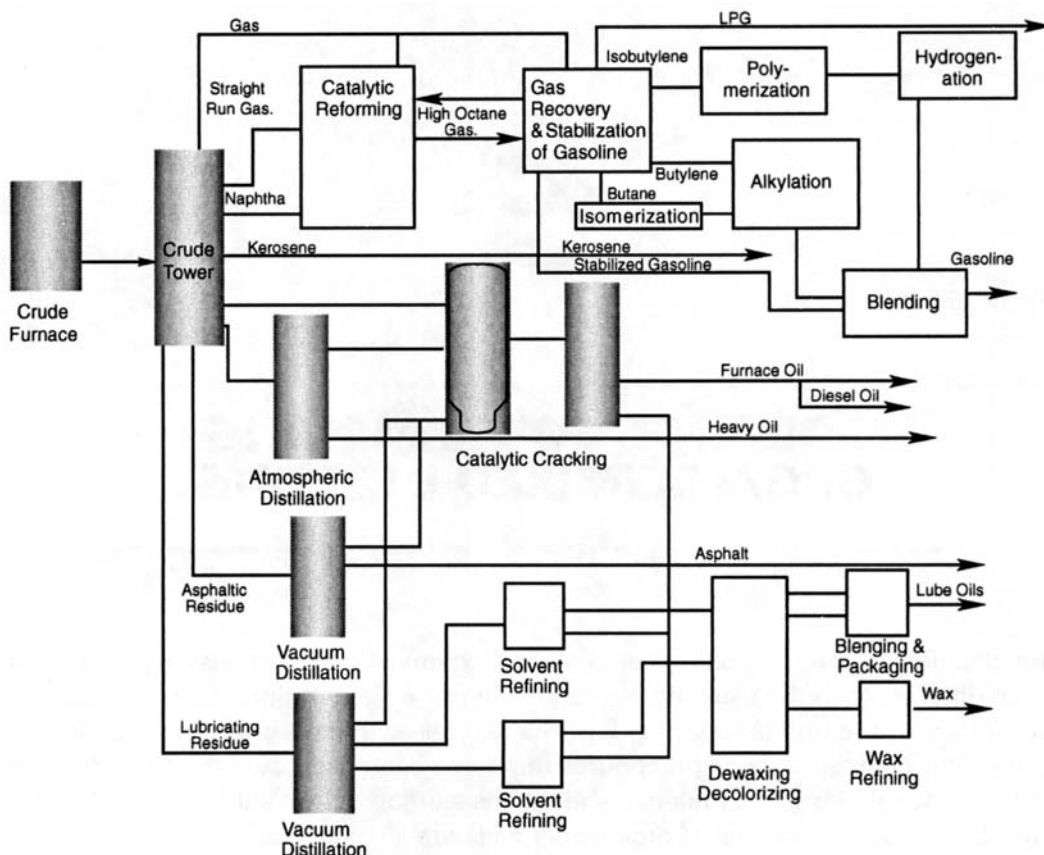


Figure 1. Generalized refinery layout.

Once the testing is completed, the crude is ready to begin its travel through the refinery. The first unit it will encounter is the *desalter* (not shown). In this unit, the crude will be washed with water to remove soluble salts and particulates. Chemicals and/or electrical charges will also be used to remove contaminants. These units can be cleaned by circulating aromatic-containing solvents,² emulsions, detergents, and acids to remove the tars and corrosion products that foul the drums. The desalter drums are very large horizontal vessels that do not lend themselves to typical circulation methods.

On leaving the desalter, the oil will go to a *crude processing unit*³, where the first actual separations will take place. The feed charge will pass through the preheat bundles, generally on the shellside, where it will pick up heat from an already processed stream. These bundles are where one type of (undesirable) refinery coke is formed. The temperatures are not great enough to form true carbon, but the deposit will still be extremely hard to chemically remove. Better success could be realized if unit operators would clean early enough, but this very seldom happens. These deposits will have a loss on ignition (LOI) of 40–100% and will contain iron of 0–50%. These bundles are normally carbon steel, but alloys are also used. These exchangers are among the most susceptible to fouling in a refinery, so up to two in-place spares may be found per bundle. A comprehensive discussion of the cleaning of refinery heat exchangers has recently been published.³

The crude will next go through a fired furnace to be heated to 650–700°F (343–371°C), and it will then go to the *atmospheric distillation tower*. Here it will be broken into four major fractions: gas and naphtha, gas oil, kerosene, and bottoms (the heavier fraction that is removed from the bottom of the tower).

Each of the fractions will be further conditioned to remove water as in the gas stream or to further “purify” the individual streams. Quite often additional towers will be used for this extra treating, with the bottoms being recycled back to the atmospheric tower.

Should heavy end processing be required, the atmospheric tower bottoms will be charged to a vacuum distillation tower, where low pressures are used to separate any lighter materials that may be present. On its way to the vacuum tower, the feed will go through another fired furnace to raise its temperature to 750–775°F (399–413°C). The products from the vacuum tower will be different grades of lube oil and bottoms that will go to a coking unit, a cracking unit, an asphalt plant, or a heavy oil upgrading process. The boiling points of heavy residuals are lowered by the reduced pressure to avoid cracking the molecules while separating the lighter hydrocarbons.

The deposits in a crude unit will vary from the coke on the preheat bundles to iron sulfide with light oils in the atmospheric tower overhead to heavy lube oils and asphalt in the vacuum towers. Most refiners are already set up to circulate hydrocarbon solvents throughout the system and to steam/air decoke the furnaces. This decoking involves passing a steam and air mixture through the product coils in the furnace to burn off the deposits. The air/steam ratio is constantly adjusted throughout this decoking to control the rate of combustion. There was success with both alkaline solutions and alkaline solutions in conjunction with hydrocarbon solvents in the low-heat areas (such as the towers). The light product condensers will contain iron sulfides with light organic coatings, and the heavier ends will contain asphaltenes and tars. Solvents up to and including concentrated sulfuric acid were used.

Metallurgy will vary from carbon steel to stainless steels to Monels. Depending on which types of crudes are being processed, there will exist the potential for naphthenic acid corrosion, hydrochloric acid corrosion, hydrogen sulfide corrosion, sulfide penetration, polythionic acid corrosion, and erosion. Therefore, it is necessary to know the conditions of these units before treating with any aggressive solvents. In general, the lighter the product, the more likely the chance for corrosion.

Generally, once the process streams leave the crude area, they will be “sweetened” in a *hydrotreater*.^{4,5} In a hydrotreater, the feed is combined with hydrogen and passed over a catalyst at elevated temperatures and pressures; the hydrogen links with sulfur to give hydrogen sulfide, and with nitrogen compounds to give ammonia. These gases are separated from the oils and are sent to other units for processing. The hydrogen may also combine with the hydrocarbon to produce a more valuable product.

The oil feed is preheated in cross exchangers to a temperature usually between 400°F and 700°F (204°C and 371°C). It then passes to a fixed-bed reactor vessel together with hydrogen-rich gas. In the reactor, the feed is treated in the presence of the hydrogen and a regenerable metal oxide catalyst at pressures usually between 200 and 1000 psig (1.37 and 6.89 MPa). After leaving the reactor, the product stream is cooled before entering a low-pressure separator. This procedure allows the removal of dissolved gases before the next stage, a stripper column, where the product is freed

from hydrogen sulfide and any light ends. Part of the reactor effluent stream may be used to supply heat to the product stripper reboiler, or steam may be alternatively used.

The next unit the oils will encounter, and possibly the most important unit in the refinery, will be the *cracking units*. These units will be catalytic cracking units, thermal cracking units, or hydrocracking units. Many refineries will have all three, with each one feeding the other or operating in parallel. The purpose of these units will be to convert high-boiling nongasoline hydrocarbons to lower-boiling gasoline components.

Hydrocracking

This is essentially a hydroformer, which operates at higher temperatures, that is, 650–800°F (343–427°C) and pressures (1200–3000 psi or 8.27–20.68 MPa). Almost all the materials in these units will be alloys ranging from Series 304 to series 430 stainless steels. The deposits will be similar to those found in hydrotreaters, such as iron sulfide and heavy organic deposits. The feedstock will be similar to heating oil. These units will generally only run in summer months.

Thermal Cracking

The thermal process was the earliest method used by refiners to produce gasoline components. High temperatures, that is, those over 600°F (316°C) and residence time were used to determine the yields of lighter products. The advent of catalytic cracking processes essentially replaced thermal cracking, but it is still used in some places. Today, thermal cracking is used mostly in coking units. There are two basic types of coking units—*delayed coking* and *fluid coking*. In delayed coking, the charge is fed directly into a fractionator where it is combined with the recycle, and it is pumped to the coke heater where it is heated, at 900–950°F (482–510°C) to produce partial vaporization and mild coking. This vapor/liquid mixture then enters the coke drum, where the vapor experiences successive cracking and polymerization until it is converted to vapor and coke.

The coke drum overhead vapor enters the fractionator, where it is separated into gas, light and heavy gas oils, and recycle oil that combines with fresh feed. These units will have at least two drums, one of which is in coking service while the other is being decoked with high-pressure water jets.

In fluid coking, the feed is pumped through a furnace where it is heated, at 1110–1200°F (599–649°C), and then it proceeds to a reactor where it is thermally cracked, at 900–1050°F (482–566°C). Products other than coke are quenched overhead in a scrubber where entrained coke is removed. The lighter fractions go overhead to be treated elsewhere, while a heavy fraction with entrained coke fines is recycled to the reactor. Coke from the reactor circulates back to the heater, and it then passes again through the reactor until it finally leaves the process unit.

Other than high-pressure jetting, there is little to offer for the process side of these units. The auxiliary systems associated with these units, especially fluid coking, offer applications for cleaning services. Emulsions of caustic and diesel fuel were used to clean a fractionator tower, and caustic foam was used to clear the air-cooled exchangers.

There are a great number of lube and seal oil systems in these units. The fluid cokers may have up to three cyclones or venturis to separate the coke fines from the overhead products. Because the products leaving these units will have to be cooled, water-side problems will occur at these temperatures (formation of iron oxides and hardness deposits will require chemical treatment). The furnace itself will be steam/air decoked, but the fuel lines will have to be periodically cleaned to reduce burner fouling.

We have followed the path of the bottom cuts from the crude processing unit. We are now left with the naphtha and gas cuts from the atmospheric distillation tower. As both these cuts leave the area, they will be "sweetened" in a hydrotreater or amine unit before being further processed.

The naphtha will go to a *catalytic reforming unit*.⁶ These units are designed to increase the antiknock quality of motor-fuel blending stocks. The principal reaction in this process is dehydrogenation of naphthenes to form aromatics. Basically, a straight-chain naphtha is heated and passed through a catalyst bed to form a ring structure. During this reaction, hydrogen is produced—some of that is recycled to sustain reactor pressure and to reduce coke formation. The rest of the hydrogen is sent off site to be used in other processes.

During desulfurization, the process streams are not very corrosive, so carbon steel or low-grade alloys are used in the construction of reformers. Because the feed is very clean to protect the catalyst, there will be very little fouling of these units. The deposits that will be present will be cyclic naphtha, which is the second type of refinery coke. These deposits require an oxidizing solution (such as chromic acid or permanganate). There may also be iron sulfides, if the upstream processes are not properly operating.

One item, which should be looked at during an outage, is the piping going through the furnaces to the reactors and the hydrogen supply and recycle lines. During an outage, these lines will oxidize and form rust. Should these lines be directly placed into service, there will be an immediate increase in pressure drop across the catalyst beds that will result in higher temperatures and reduced flow rates. Because these lines will generally not stand a complete liquid fill, foam or vapor phase cleaning should be considered. The catalyst regeneration piping will also fall in this category.

Other fouling problems in a reformer will be the lube oil system on the hydrogen recycle compressor and the cooling water systems. The fuel lines on the furnaces will also eventually foul.

The product from the reformer will be blended with the products from the alkylation units to make gasoline. These *alkylation units*⁷ are the units that process the gas fraction of the crude oil. These units use a catalyst to combine olefins, paraffins, or aromatics to form a high-octane product to blend into gasoline. There are two types of alkylation units that derive their name from the catalyst used: sulfuric acid and hydrofluoric acid.

In the *sulfuric acid alkylation units*, the feed is mixed with a recycle stream of acid and is fed to the contactor. The liquid contents of the reactor are circulated at high velocities, and an extremely large amount of interfacial area is exposed between the reacting hydrocarbon and the acid catalyst. The entire volume of the liquid in the contactor is maintained at a uniform temperature. In fact, the maximum deviation between any two points within the reaction mass is less than 1°F (−17°C). The hydrocarbon/acid emulsion proceeds to a settler, where gravity separation of the hydrocarbon from the acid occurs. The settled acid is recycled to the contactor.

The light ends are flashed off, washed, and sent off site. The bottoms will also be washed (separately) and will go to the deisobutanizer tower. The overhead from the deisobutanizer and effluent refrigerant cycle normally constitute the total isobutane recycle to the reaction zone. The isobutanes and all other hydrocarbons are maintained in the liquid phase as diluents throughout the reactor, thereby serving to promote the alkylation reaction.

There are several units in a sulfuric alkylation system that can be cleaned. The depropanizer tower will probably contain iron sulfides that can be removed by an acid/aldehyde⁷ solvent. There will also be sludge in the acid storage tank and the caustic wash tank that can be cleaned by high-volume flushing or by a rotojet. The best opportunities will be in the cooling water system and the refrigeration system. The refrigeration system will be cleaned and dried before initial startup, but a seal oil leak into the system may necessitate operational servicing. In general, all these operational deposits can be removed by a degreasing solution followed by acid or chelant. An emulsion solvent of a hydrocarbon with an acid should also be necessary. Most scale in these units will generate a dilute acid and heat on contact with water, so care should be taken when filling, pressure testing, and so on.

The process flow of an *HF alkylation*¹ unit is somewhat similar. The inlet charge is intimately mixed with the HF catalyst and then goes to a settler. The acid phase is recycled to the reactor; occasionally, a small portion is regenerated. The settler overhead product is freed of isobutane and lighter components in the isostripper, the bottom product of which is a motor blending alkylate. A portion of the isostripper overhead vapors is depropanized, and the propane is freed of acid in the HF stripper. The deposits will be iron fluorides and, very infrequently, iron oxides (the fluid usually is too acidic for oxides to form). Dilute HCl is generally used to clean these units. The addition of boric acid will sometimes aid the treatment. The

TABLE 1

Deposits/Solvents in Units not Considered in Detail in Other Sections

Unit	Deposit	Solvents
Crude	Coke, mixed FeS, paraffins	NaOH, TSP, sodium metasilicate, acid/aldehyde, aromatic naphtha
Towers	Mixed organic	Emulsions, H ₂ SO ₄
Overhead condensers	Mixed organic	Emulsions, solvents
Preheat exchangers	Coke, FeS, mixed organic	NaOH, TSP, sodium metasilicate, acid/aldehyde, aromatic naphtha
Coking units	Coke, mixed organic	NaOH, TSP, sodium metasilicate, emulsions
Cat reforming	Coke, FeS	Chromic acid, alkaline, acid/aldehyde, permanganate
H ₂ SO ₄ alkylation	FeS, Fe sulfate	Acid/aldehyde, alkaline
Depropanizer	Iron sulfide	Chelants, emulsions, acid/aldehyde
Cooling water	Hardness, iron	Chelants, acids
HF alkylation	FeF ₃ , oils	HCl, reducing agent, boric acid

cooling water system and lube and seal oil systems will also have to be periodically cleaned.

This concludes the major units in a refinery. There is one major auxiliary unit in a refinery that requires cleaning. This is the *amine unit*.^{9,10} While there are many processes to remove H₂S and/or CO₂ from gas streams, the most widely used are the amine systems that depend on the reactivity of H₂S with amino nitrogen for their absorption properties. The most currently used processes today are monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), and diisopropylamine (DIPA). Deposits/solvent related to units described above that are not to be considered in more detail are given in Table 1.

SPECIFIC PROBLEMS IN HYDROTREATING UNITS

Hydrofining is one type of hydrotreating. The feed is combined with hydrogen and is passed over a catalyst at an elevated temperature and pressure (see Figure 2).

Consumption of hydrogen imposes one of the major costs for hydrotreating. The hydrogen links with sulfur-bearing compounds to give hydrogen sulfide and saturated hydrocarbons. Hydrogen also unites with nitrogen-bearing compounds to give ammonia. Then, the hydrogen sulfide and ammonia are scrubbed from the light hydrocarbon stream to be disposed or separately recovered.

For catalytic reforming, hydrotreating is a must. The reforming catalyst is susceptible to poisoning by sulfur, nitrogen, and metal compounds in reformer feed. Without

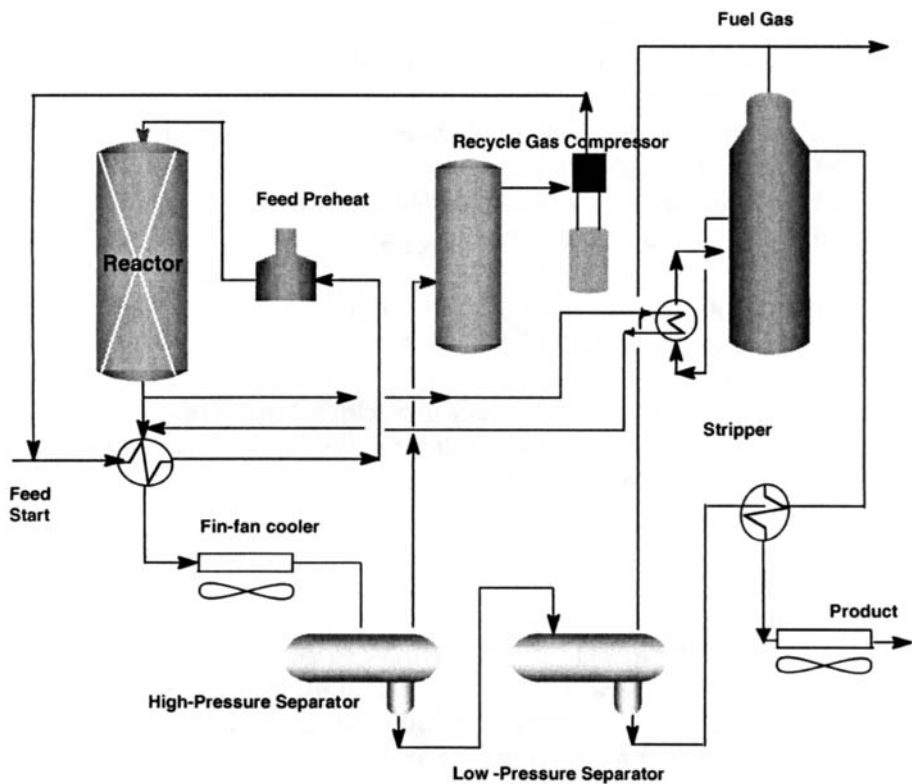


Figure 2. British Petroleum Hydrofiner.

pretreatment, the catalyst life would be greatly reduced. Therefore, treating reformer feed is justified by longer reformer catalyst life, longer time between regeneration cycles, better reformer yields, and better reformat quality.

Catalytic cracking is another process to benefit from hydrotreating. The benefits are similar to those for reformat pretreatment: longer runs, better cracking selectivity, and better product quality. Another advantage is reduced sulfur laydown on the cracking catalyst. Then, catalyst regeneration will contribute less sulfur dioxide to the atmosphere.

Preheat Bundles

These bundles will have the feedstock on one side and the reactor effluent on the other side. The amount of preheat given to the feed is directly related to how hard the furnace has to be fired. It is also related to the coolant required to bring the temperatures down so an efficient removal of unreacted hydrogen can take place.

These bundles are generally carbon steel and will become fouled with salts (primarily ammonium chloride) and iron sulfide. These bundles will have been presulfided over rusty metal, so substantial amounts of iron sulfide can be found. Inspections have found up to 170 lb (77.11 kg) of iron sulfide per 1000 ft² (92.9 m²), but the average appears to be around 40–60 lb/1000 ft² (18–27 kg/92.9 m²). It should be noted that the iron sulfide deposits found will be determined by two factors: location of the hydrogen addition and flash point of the process stream.

The product being hydrofined will have been separated somewhere upstream. The stream, which comes off the top of the fractionator, will have the greatest amount of sulfides. As the H₂S is made after the hydrogen introduction, those areas downstream of the fractionator will have the majority of the iron sulfide.

Generally, these bundles will be cleaned for heat transfer, but some have reported excess pressure drop. These cases were almost always due to the salts and can be solved by steam and/or water injection. These bundles can usually be chemically cleaned. To date, only NaOH, TSP, sodium metasilicate, surfactants, and acid/aldehydes were used. An acid/aldehyde/hydrocarbon emulsion also can be used to clean these units.

After cleaning, these bundles should be dried as soon as possible and laid up under nitrogen until they are presulfided. This will allow the sulfide layer to be laid down on an active surface. Sometimes the bundles are divided into hot and cold effluent bundles. The hot effluent bundles will be closest to the reactors, and probably will be made of a high chrome alloy or austenitic stainless steel. These can be cleaned in the same way (also see Reference 3).

Furnace

The furnace is used to further heat the feed before it enters the reactor. The tubes will always be an alloy. We have found these tubes to vary from 1% Cr alloys to Series 321 stainless steel. The furnaces can be cleaned by the same method as outlined in the section on preheat bundles, but care should be taken to ensure that no coke or iron disulfide is present, as both of these deposits are not soluble in the aldehyde/acid solvent used to dissolve FeS. If the furnace is coming down, then the reactor also will be taken off line. In this case, the reactor will be regenerated. The furnace will be used

for heat and will contain little if any coke. This “steam–air decoking” procedure will also oxidize the disulfide to water-soluble sulfate. We have found scale loadings to be as high as those found on the preheat bundles.

Also on the furnaces are the fuel lines that will eventually foul. Increased pressure drop and frequent cleaning of the burner tips are good indications of fouling. The organic phase can be removed by alkalis or by various products sold for this purpose. Iron sulfide will generally be present, because the stripper gas may be used as fuel gas. In this case, an acid/aldehyde emulsion may be desired. Drying is also required to keep the metal from rusting, flaking, and plugging the burner nozzles.

Reactors

Reactors are almost never cleaned (except by specialized catalyst handling companies). The catalyst is normally kept dry. Heavy metals are present, which will be picked up by the solvents, and can be regenerated or sold. The reactor volume may equal the total of the rest of the system.

Hydrogen Recycle System

The deposits found here are primarily inorganic and usually are iron sulfide, iron bisulfide, or iron oxides. Quite often a combination of all three is found. This can be the most fouled part of a hydrofiner, as the metals are of lower alloys and there will be very little instrumentation on these systems. One refiner found his problem when he could not close his valves to bring down the unit. Considerable iron bisulfide also may be present. The compressors will have lube and seal oil systems that will also require cleaning.

Stripper

Strippers may or may not have accumulators on both the overhead and bottoms. These vessels will be constructed of a high alloy, as this is the “sourest” part of the unit (i.e., containing the highest amount of sulfur compounds). Titanium and Series 400 stainless steels are not uncommon. These vessels will have some type of lining such as gunite, so extreme care must be taken before these vessels are chemically cleaned.

The primary deposit will be iron sulfide, and some coke may be found above the stripping steam inlet. The drums may have an accumulation of sludge, if the bottom connections extend into them. Overhead drums are susceptible to corrosion as a result of the water/H₂S mixture, so if possible check this vessel before cleaning to determine if FeS is present. Copious amounts of ammonia were also found in the linings of these drums, so care should be taken when water flushing, and so on.

Coolers

The air coolers and the water-cooled exchangers will require cleaning. This can be done by standard methods, provided there is no leakage of the product into the water-side. Table 2 summarizes classical methods for cleaning some parts of hydrotreater units.

TABLE 2

Deposits/Solvents in Hydrotreaters

Component	Deposit	Solvent
Preheat bundles	NH ₄ Cl, FeS, organic	NaOH, TSP, sodium metasilicate, surfactant, acid/aldehyde, emulsions
Fuel lines	FeS, organic	Acid/aldehyde, emulsions, alkaline solvents
Stripper	FeS, coke	Acid/aldehyde, emulsions, alkaline solvents
Furnace	Same as bundles	Acid/aldehyde, emulsions, alkaline solvents
Hydrogen recycle	FeS, iron oxide, FeS ₂	Acid/aldehyde
Coolers	Iron oxides, hardness	Chelants, HCl

SPECIFIC CLEANING PROBLEMS IN CATALYTIC CRACKING UNITS

Catalytic cracking (see Figure 3) is a refinery process to convert high-boiling non-gasoline hydrocarbons into lower-boiling gasoline components. The catalyst may be in a fixed bed, moving bed, or fluid bed. Activated natural or synthetic catalysts (primarily silica alumina or silica magnesia) are used in bead, pellet, or microspherical form. See Table 3 for solvents and deposits in catalytic cracker units.

Feedstocks may range from naphtha cuts (included in normal heavier feed for upgrading) to reduced crudes. Usually, feed preparation (to remove salts and heavy asphalts) is performed through any one of the following ways: coking, propane deasphalting, furfural extraction, vacuum distillation, viscosity breaking, thermal cracking, and hydrosulfurization.

Products

The major products of catalytic cracking are olefinic gases that are useful for polymerization or alkylation, cracked gasoline, and catalytic cycle oil.

The catalytic cracker is one of the largest producers of "sour water" in the refinery. This sulfur-containing water forms in the steam strippers and overhead accumulators on the product fractionators. The major by-products resulting from catalytic cracking operations are oil, sulfides, phenols, ammonia, and cyanide.

The Feed System

This is only meant to include the piping and exchangers inside the boundary limits of the catalytic cracking unit. A hydrotreater will generally be in front of the cracking unit, but information on this unit is covered elsewhere. The feed system will be mainly composed of carbon steel piping and exchangers; however, sometimes a furnace will be used to preheat the feed and will be made of an alloy.

This area has to be preoperationally cleaned to remove particulates and iron oxides. In addition to being a dehydrogenation catalyst, iron is also an oxidation catalyst and promotes the conversion of CO to CO₂ in the regenerator. This conversion is

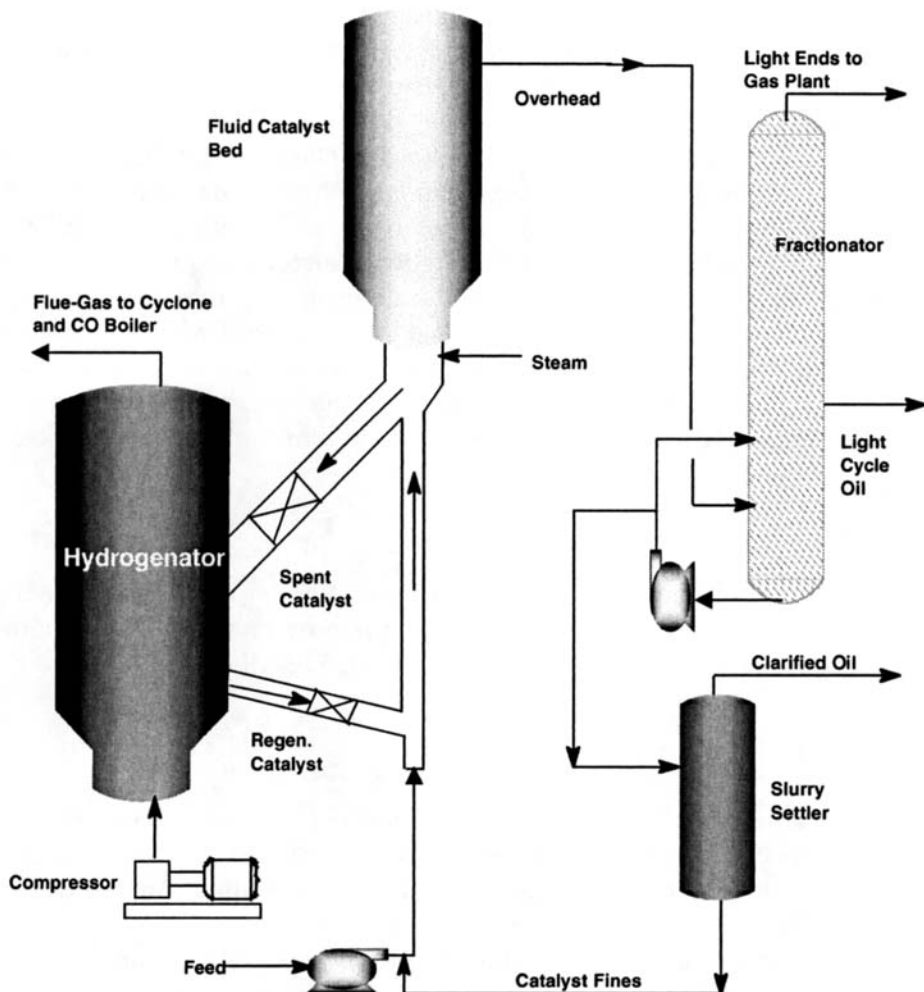


Figure 3. Fluid cracking unit.

termed “afterburning” and is very undesirable because of the large amounts of heat released in those areas that are not meant to handle it. Iron is also known as a catalyst poison.

This area will also require operational cleaning, because refiners generally operate at maximum preheat. This lowers coke production, increases other yields, and

TABLE 3
Deposits/Solvents in Catalytic Crackers

Major Components	Deposits	Solvents
Feed system	Iron oxide	Chelants (preop), HCl
Heat exchange	Light coke	Diesel with surfactant
Bundels	Mixed deposits	Emulsions
Carbon monoxide (CO)	Iron oxide	HCl, chelants
Boilers	Hardness	HCl, chelants
Sour water lines	FeS	Acid/aldehyde
Steam lines	Iron oxides	HCl, chelants

increases unit capacity. For this reason, cracking units will have in-line spares for critical bundles, and these bundles will very frequently be cleaned. Thankfully, these bundles are also relatively easy to clean, as long as they have not been fouled to the point of plugging.

Generally, the only bundles that will be hard to clean will be those between the bottom of the fractionator and the reactor. These units may be coked if the process was upset. The other bundles can be cleaned by first circulating the light cycle oil, which is a cut off the fractionator. Diesel fuel may also be used. The addition of a surfactant to the diesel will help disperse the deposits, but more than one system volume will probably be needed. An emulsion can be used with the last stage to remove iron oxides. If the acid is the inner phase, passivation may not be required. If the cleaning stages are separate, or if the organic is the inner phase, then ammonium citrate is recommended for passivation because sodium is also a catalyst poison.

CO Boilers

These units should be treated just as a normal boiler, both operationally and preoperationally. They will have fans, feedwater systems, and perhaps a superheater. These have been known to generate up to 1000 psi (6.89 MPa) of steam.

Lube and Seal Oil Systems

A very important part of a cracking unit consists of the lube and seal oil systems. In addition to the pumps and boiler uses, a cracking unit will have large systems for the air compressors and cyclone separators, which these units contain. Systems of up to 6000 gal (22,710 L) are not uncommon.

The *air lines* in a cracking unit should be preoperationally cleaned, both on the suction and discharge of the compressors. These units use large amounts of air, so velocities are high. Any particles in these lines can ruin the compressors or valves. Any iron will also poison the catalyst and may contribute to afterburning. Individual designs will dictate which method of cleaning will be required. It is possible to operationally clean the lines should the pump oil seals leak, but it is not generally done.

The *steam lines* on the boilers should be cleaned as in a normal utility boiler. There are also steam lines, which bring in steam from outside the unit area to start the unit. This steam will be used to preheat the reaction area and to turn the compressors. During operation, steam is also used to strip undesirable products from the catalyst before entering the regeneration suction. Steam or water sprays may also be used at the top of the regenerator to cool this area. This excess heat can be generated either by afterburning or will be present if no CO boilers are used and the catalyst is burned with excess air.

The lines have to be cleaned to prevent particulate damage and to keep iron from contaminating the catalyst. These lines are generally "blown" with steam or air, but this procedure causes problems with energy requirements and other personnel in the area.

There will generally be no chemical cleaning involved in the *fractionator, cyclone separator, slurry settler, reactor, or regenerator*. These areas will have coke, catalyst fines, and heavy sludge that can best be removed by hydrojetting.

These cracking units will also have cooling water exchangers and/or air coolers as trim coolers on the fractionator overhead. These have to be maintained, as the overheads will have the highest dollar value to the unit. There are also other units associated with cracking units. The feed will generally be hydrotreated to remove metals, sulfur, and organic nitrogen that will poison the catalyst.

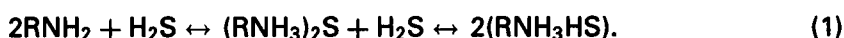
There will also be sour water lines from the steam stripping. These extra systems will require an amine system and a sulfur recovery area, but they may not be down with the cracking unit because more than one unit may operate with these auxiliary units. These auxiliary units can usually be cleaned with an acid/aldehyde solvent. Table 3 reviews specific solvents used to clean catalytic units.

SPECIFIC CLEANING PROBLEMS IN AMINE SYSTEMS

While there are many processes for removing H_2S and/or CO_2 from gas streams, the most widely used are the amine systems. These systems depend on the reactivity of H_2S with amino nitrogen. The most currently used processes today are MEA, DEA, DGA, and DIPA. Diglycolamine is a trademark of the Jefferson Chemical Company; the others are chemically accurate in referring to the structure of the compound.

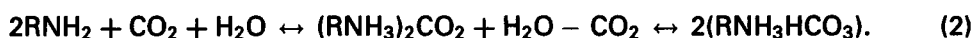
The following reactions are given.

With H_2S ,



This reaction proceeds to the right at low temperature and high H_2S partial pressures. For this reason, the absorption is normally conducted at pressure of 300 psi (2.06 MPa) or higher and at or near ambient temperature. Regeneration is normally performed at or near atmospheric pressure and at the solution boiling point.

With CO_2 ,



The MEA is by far the most widely used of these compounds. It is a clear, colorless liquid that boils at 338°F (170°C) at atmospheric pressures. Of all the amines used, it is the strongest base and so reacts most readily with acid gases.

The processes are basically the same with little variation in flow scheme. The sour gas containing H_2S and/or CO_2 enters the plant through a scrubber, which removes any free liquids and/or entrained solids. The sour gas then enters the bottom of the absorber and flows upward in countercurrent contact with the descending aqueous amine solution. Sweetened gas leaves the top of the absorber and flows to a dehydration unit, where saturation water from the aqueous amine solution is removed.

Need for Cleaning and Deposits Present

As these units are self-circulating, they can be cleaned by using the system's pumps. These units operate on a pressure differential so some inert gas will be needed. These units should be preoperationally cleaned. Oils, greases, and particulates will cause foaming of the amine by affecting surface tension. The resulting foaming will cause a loss of the amine off the top of the stripper. While some iron sulfide will be formed during operation, a smooth, passive surface will reduce the

amount formed. Removal of iron oxides will also generally mean fewer filter changes during startup and less chance of particulates dropping out in low flow areas. Iron oxide particles in the solution may also combine with sulfides during operation and possibly form ferrous sulfide in the stream that will turn the amine black.

Filtration of the cleaning solutions should be done either by using system filters or by using auxiliary filters. The amines themselves are good degreasers, so quite often the customers will circulate the systems themselves in an effort to clean them. The amount of amine lost as a result of foaming and carryover will quite often be in the price range of the chemical cleaning.

These units can also be cleaned for operational deposits. Because the amines are water soluble, these systems may not require a degreasing stage. However, some product will have entered into the system and should be removed, but this should be handled on a case-by-case basis. Once the organic deposit has been removed, an acid/aldehyde mixture should be used as the solvent.

The entire unit should be cleaned to avoid contamination of the fresh amine, but the customer may not feel the need to do this. As a minimum, the stripper overhead, amine/amine exchangers, and water-cooled exchangers between the towers should be cleaned.

The stripper tower separates the acid gases from the amine systems, and so its efficiency dictates how effective the system works. Increased pressure drop caused by fouling means higher firing on the reboiler. This condition may lead to corrosion and more amine lost through carryover.

The cooler on the overhead system of the stripper tower controls the quantity of water and amine that is recovered from the overhead streams. This may be an air- or water-cooled exchanger or combination of these. These must effectively cool if excessive amine is not to be lost. These exchangers will also affect downstream corrosion, because the corrosivity of these acid gases is definitely increased by increasing temperature.

The amine/amine exchangers and the water-cooled exchangers have a great deal of effect on the operation of the system. As the absorber runs cool and the stripper runs hot, these exchangers must be efficient to exchange the heat. The amine/amine exchangers play a large role in the corrosion found in the stripper tower and reboiler.

The stripper reboiler should be cleaned to lower the energy required to heat the amine and to control internal corrosion. High skin temperatures on the reboiler tubes will greatly increase the reaction rates of the acid gases.



The outlet pressure will be ~400 psi (2.75 MPa).

The second way to manufacture hydrogen is by partial oxidation. This process starts with oxygen or air that is mixed with steam and either a natural gas or a liquid hydrocarbon as the fuel. The free oxygen reacts with the fuel to produce CO₂ and water vapor. A secondary reaction between the gases will form hydrogen and CO. Both of these reactions are exothermic. However, in the case of liquid feeds, steam will have to be injected into the reactor. Temperature in the reactor will be around 2500°F (1371°C) and up to 1500 psi. Once the process stream leaves the reactor, it will go to shift converters and purification areas just like the steam reforming method.

The primary areas for application of cleaning services are the water areas of these plants. The *waste steam system* can generate 900°F (482°C) superheated steam

and will quite often be tied into a manifold with a steam-generating unit inside the furnace. These units will have drums, blowdown, piping, superheaters, and so on, like a conventional boiler. Because the process stream will be very hot, higher Cr/Ni alloys may be used, and so a complete check on the metallurgy will have to be done. These systems will have to be preoperationally cleaned as well as periodically operationally cleaned. Care should be taken, as the catalyst base was found to be dissolved by steam in certain cases and has ended up in the waste steam system.

Cooling water is important in these units as the reactions are mainly exothermic and have to be cooled between stages. Because the temperatures are high, air-cooled exchangers will provide much of the cooling, but water may be used for tempering. Certainly, the *air-cooled exchangers* will have to have the air side cleaned on a regular basis.

The desulfurizing *amine system* will have to be preoperationally and operationally cleaned. Please see the section on amine systems for the discussion of cleaning these units. Certainly, the CO₂ removal amine unit will have to be preoperationally cleaned to prevent excessive foaming. Recently, Gutzeit published a comprehensive planning guide for the cleaning of refinery and chemical processing equipment.¹¹ This book describes many of the known cleaning techniques in much more detail than can be provided in this review.

JOB DESIGN CONSIDERATIONS

If a chemical cleaning job fails to achieve the desired results, the cause usually is poor job design and not improper chemistry. The chemistry cannot be effective unless the solvent reaches the deposits at the proper temperature to allow dissolution to take place and is constantly replenished. Important job design considerations are as follows. The first is flow rate. There must be enough flow to fill and circulate all portions of the unit being cleaned. The hoses, inlets, and outlets must be sized appropriately with the available pumps. The second is venting. If the cleaning process can produce gas (such as H₂S while dissolving FeS), the system must be able to vent this gas. The third is flushing and drains. Most solvents will leave undesirable films on the cleaned surfaces unless they can be flushed with fresh water or a passivating solution. The fourth is heating and cooling. During cleaning, the heat exchange system can be heated with an external heat exchanger, with process fluids, by direct firing, or by use of injected steam or plant-supplied hot water. Any of these methods can be successful. The key is to maintain the solvent at its optimal cleaning temperature for the duration of the job without overheating, which could cause excessive corrosion or solvent degradation. The fifth is disposal options. Each plant location (and some individual units within a plant) can have different chemical disposal requirements (see the next chapter for some general options). The disposal options must be considered and become part of the cleaning plan *before* the solvent (or mechanical option) is chosen. The cost of the disposal frequently exceeds the cost of the cleaning operations. For example, Radtke (Reference 16 of the next chapter) described the waste treatment procedures required to process chemical cleaning wastes generated during the cleaning of a nuclear steam generator. The cleaning phase lasted about 2 weeks but the waste processing took 3 months. This is an extreme example, but it illustrates the importance of considering waste disposal during the planning phase of any cleaning operation.

REMOVAL OF IRON SULFIDE DEPOSITS

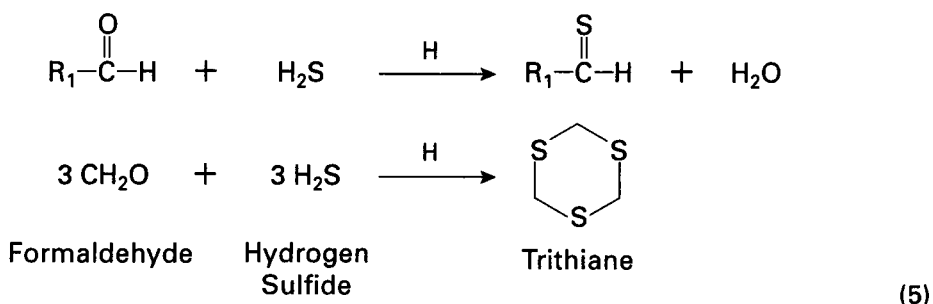
In many of the hydrocarbon processing steps, iron-based surfaces may come into contact with sulfur-containing fluids. At the temperatures present in the various reactors, and during long periods of contact, iron sulfide deposits (generally FeS, but sometimes FeS₂) will form. The cleaning of FeS deposits is such a dangerous operation that a separate section is devoted to the literature found to describe the known technology.

The reduced sulfides can be easily dissolved by using mineral acids:

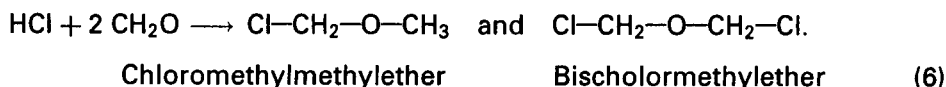


While this is a very effective procedure, it produces large amounts of toxic hydrogen sulfide. This gas produces severe safety and operational problems. Lawson et al.¹² reviewed the major procedures for safely removing iron sulfide deposits: (1) mineral acid with an acid/gas scrubber; (2) mineral acids with hydrogen sulfide suppression chemicals; (3) multiple stages of oxidizing agents with acids; and (4) alkaline cleaners. If none of the suppression/control technologies is used, the vessel being cleaned must be vented through an NaOH scrubber with enough capacity to absorb all of the hydrogen sulfide during the shortest possible reaction time. As an alternative, the vessel can be vented to a flare. In both cases, it is advisable to vent through a knockout tank to remove any entrained liquid.

Several different suppression technologies are available. Frenier et al.,⁸ Ball and Frenier,¹³ Buske,¹⁴ and Frenier¹⁵ developed suppression agents that contain aldehydes. The most efficient agent is formaldehyde that stoichiometrically reacts with hydrogen sulfide to produce trithiane, a very insoluble material. Sometimes, a backup scrubber system also is used to ensure complete removal of sulfide gas (Figure 4).



Tests conducted in the laboratory, and backed up with treatments, demonstrated that formaldehyde used with sulfuric acid can dissolve FeS with essentially 100% suppression of H₂S evolution. There are several problems with the use of formaldehyde. This chemical is listed on several compilations of suspected carcinogens. In addition, formaldehyde can react with hydrochloric acid to form chloromethyl ethers,¹⁶ which are known human carcinogens.



Because of concerns about formaldehyde, this chemical was replaced by glyoxal. The chemical, glyoxylic acid,¹⁴ also can be used with hydrochloric and sulfuric acids.

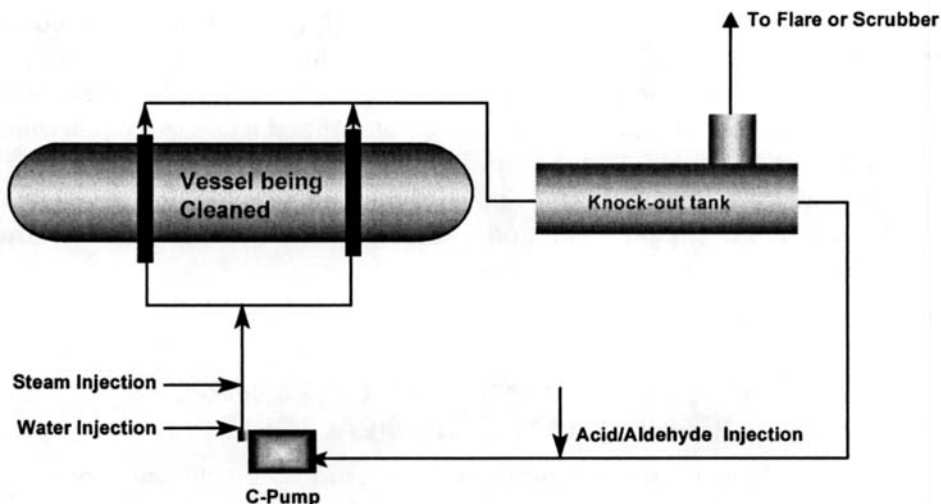
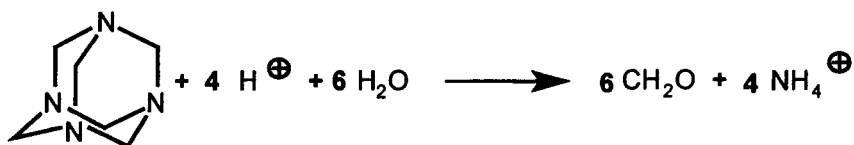


Figure 4. Setup for aldehyde H₂S suppression.

Formaldehyde can also be generated in situ by adding hexamethylenetetramine to strong acid.

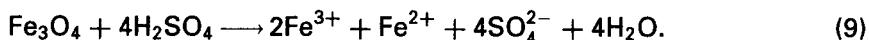
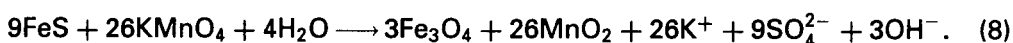


Hexamethylenetetramine

(7)

A system using maleic acid was invented by Lawson¹⁷ to suppress hydrogen sulfide during the removal of iron sulfide. Tests showed that >90% suppression of H₂S could be achieved while 65% of the FeS was dissolved.

In the previously cited work,¹² Lawson suggested alternate stages of potassium permanganate and sulfuric acid for removing FeS.



A nonacidic technique uses alkaline chelating agents, such as ammonium EDTA¹⁸ and oxalic acid, to dissolve as much as 3% FeS (in 100 mL) at a temperature of 300°F (148°C). The pH was about 9. The high alkalinity suppressed the evolution of hydrogen sulfide and allowed the solvent to dissolve most of the FeS.

While procedures for cleaning the tubulars of oil wells are physically different than those used in an industrial environment, the chemistry required is very similar. Several sulfide control techniques used in the oilfield are reviewed. Hall¹⁹ considered a number of precipitation control methods for sour and sweet wells. This type of precipitation is not a significant problem while cleaning industrial equipment, since the acids usually are not completely spent on the deposit. He advocated the use of a "sulfide modifier," NTA, and ethyleneglycolmonobutyl ether (EGMBE) to treat sour wells containing iron. Dill²⁰ claimed a combination of a chelating agent (NTA) and an aldehyde (aldol) for controlling iron and sulfur precipitation. Walker²¹ expanded on

this concept in an SPE paper and noted that iron control agents are not required during tube clean-out procedures, but advocated use of a “sulfide scavenger.” This material apparently is the “sulfide modifier” endorsed by Hall (above). Ford²² discusses the various types of iron sulfide found in wells and notes that the FeS (nominal) minerals are soluble in HCl, but the FeS₂ types are not acid soluble. He also advocates well clean-out procedures using only the acid and the sulfide scavenger. Williamson²³ claimed the use of a chelating agent and a ketone for the same types of treatments used by Walker.

NEW DEVELOPMENTS FOR CLEANING REFINERY/PETROCHEMICAL UNITS

Concerns about the use of toxic organic solvents prompted the development of alternative technologies to remove organic deposits. Formulations containing terpene solvents (such as *d*-limonene) were patented by Matta²⁴ to remove hydrocarbon deposits. These compositions include a terpene solvent, propyleneglycol ethers, and surfactants in a water base. They are claimed as hard surface cleaners that will dissolve oils, asphaltenes, and heavy oils. Patents by Mehta and Krajicek^{25,26} and Krajicek et al.²⁷ described processes that use terpenes and surfactants for cleaning and decontaminating refinery vessels, and for removing benzene to allow maintenance to take place. An alternate technology that contains enzymes and *N*-oxide type nonionic surfactants was claimed by Mestetsky^{28,29} as a solvent that easily releases the oil for enhanced separation and disposal of the wastewater. The documents noted above demonstrate that more ecologically acceptable and safer (compared to aromatic solvents and chlorinated hydrocarbons) methods to clean refinery equipment are being developed. Some lower toxicity chemicals are seen in Figure 5.

Lawson and Snyder³⁰ developed a solvent to remove heavy asphaltic materials. The composition consists of a heavy aromatic solvent and a compound with fused heterocyclic rings, which improves the cleaning provided by the organic solvent. Benzamidizole is an example of the fused ring compound.

Table 4 summarizes types of foulants and generalized solvents to remove them based on the most recent technology that emphasizes low-toxicity solvents and surfactants. Figures 6 and 7 show some places where these types of deposits may be found along with the generic solvent selection.

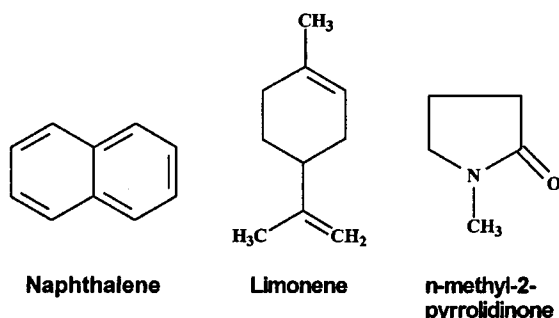


Figure 5. Environmentally acceptable solvents.

TABLE 4

Organic Deposits and New Solvent Types

Foulant	Deposit Type	General Cleaning Solvents
F1	Light hydrocarbons, C1-C5	Degassing and light-oil removal by detergents
F2	Gasoline, diesel and fuel oils, C4-C5	Degassing and light-oil removal by detergents
F3	Motor oils, greases, bunker C, crude oil	Remove with alkaline detergents and light solvents
F4	Tar and asphaltic deposits	Solvents followed by alkaline detergents
F5	Black, hard solids with a polymer matrix	Alkaline detergents, organic solvents with accelerators
F6	Black, hard solids with a coke matrix	Mechanical methods
F7	Linear polyolefins	High temperature oils or solvents followed by detergents
F8	Cross-linked polymers	Mechanical methods
F9	Paints, coatings	Alkaline detergents, solvents
F10	Cosmetic cleaning	Acidic or alkaline detergents

IDENTIFICATION OF REFINERY DEPOSITS BY FTIR

Industrial chemical cleaning uses a broad range of techniques and technologies to reduce capital, time, and costs associated with refinery and petrochemical equipment repair and maintenance. In the broad sense, chemical cleaning addresses the removal of organic and inorganic deposits or films from any internal or external equipment surface. This section will provide information on the application of an analytical technique, Fourier transform infrared (FTIR) spectrometry, to aid in the identification of organic deposits or films. This information may be used in the development of chemical cleaning formulations and methods for the subsequent removal of such deposits or films. Curtis and Weaver described the uses of this very promising technique.³¹ The remainder of this chapter was abstracted from the Corrosion/98 paper and used with their permission.

Identification of Classes of Organic Compounds by FTIR Spectrometry

The first step in this fingerprinting process is the separation of component materials from the composite sample. Once separated, the functional groups or class of the component materials may be identified by FTIR spectrometry. This separation may be affected by either physical or chemical means.

Separation by Physical Methods

One of the more common examples of physically separating components in a refinery or petrochemical soil is based on the material's volatility relative to

F1	light hydrocarbons: C1 - C5	degassing & light oils removal by detergent
F2	gasoline, diesel, & fuel oils: C4 - C15	degassing, oil & grease removal by detergents
F3	motor oils, greases, bunker C, crude oil, etc.	oil & grease removal followed by alkalis & zdetergents

DESALTING AND FRACTIONATION

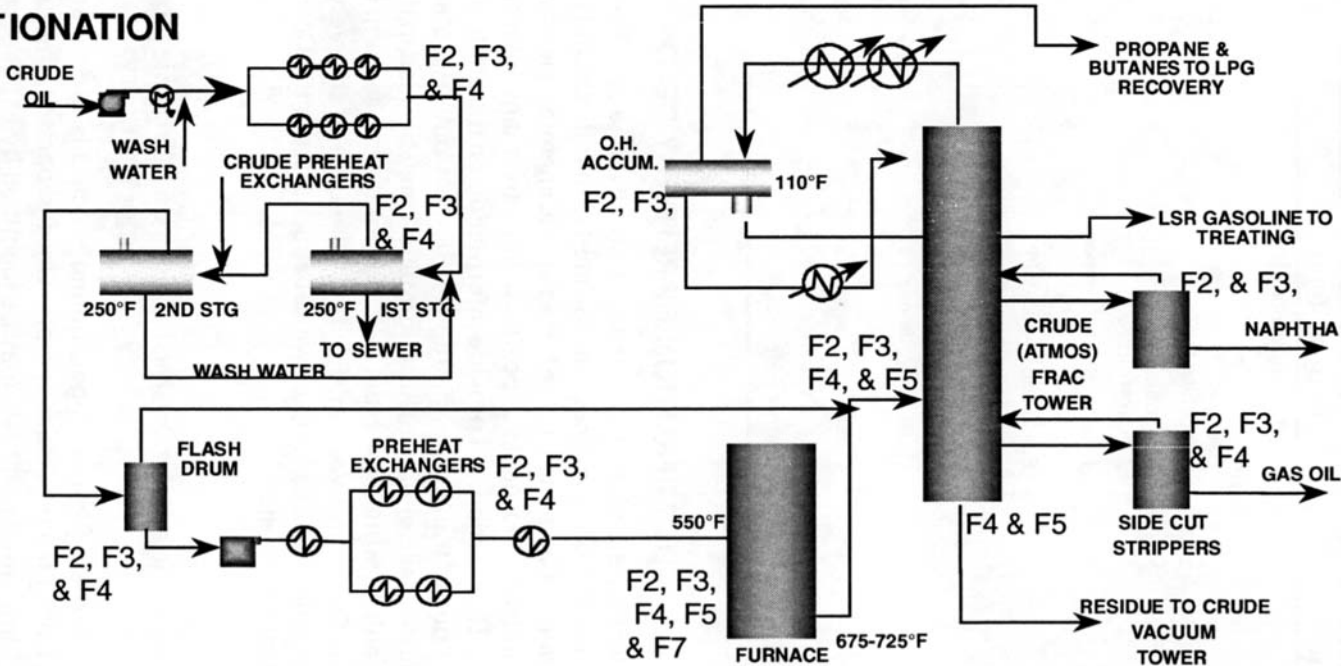


Figure 6. Refinery deposits and new solvents, 1.

F4	tar, asphalt, etc.	solvent thinning followed by alkalis & detergents
F5	black hard solid with polymer matrix	alkalis & solvents, accelerators
F6	black hard solid with coke matrix	mechanical removal or burning
F7	linear polyolefins, high mol. wt.	H.T. stable oil followed by detergent

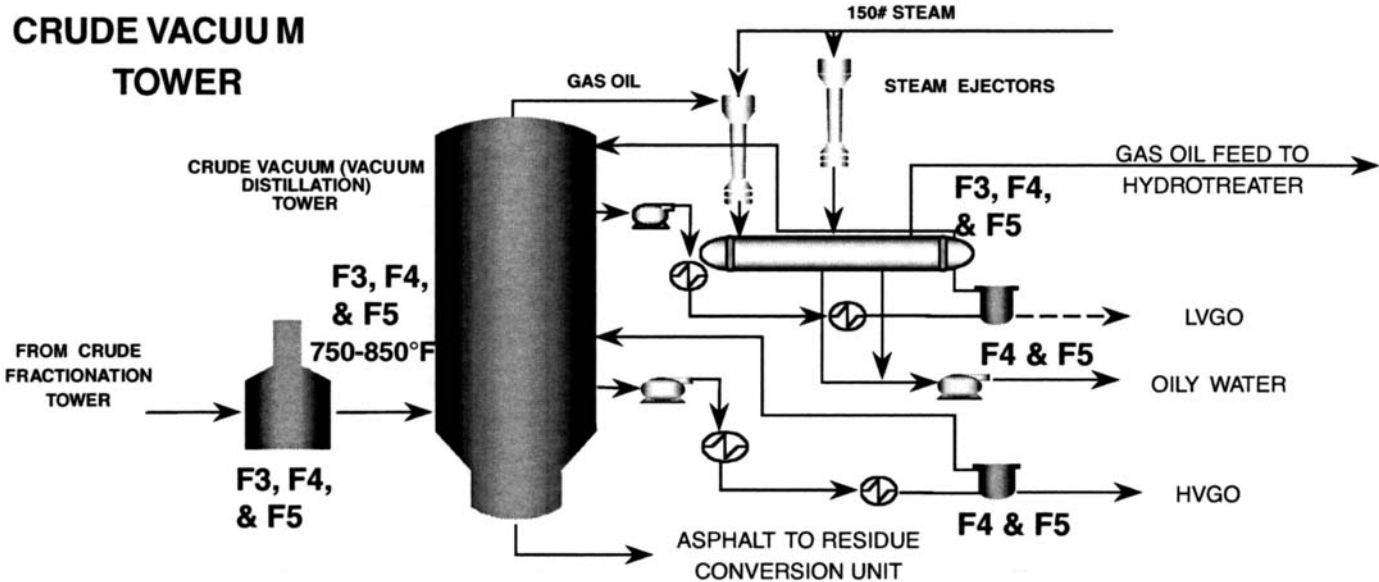


Figure 7. Refinery deposits and new solvents, 2.

temperature. By increasing the temperature by using an infrared lamp, heat gun, or other heat source, lower boiling materials will volatilize from the sample. At temperatures near or below the freeze point of water, often higher boiling materials will "gel" or "solidify." Once solidified, these materials can be removed by filtration or other suitable means. By analyzing the materials obtained from these physical separations, a better understanding of the nature of the organic materials within the sample is achieved. By electronically subtracting the FTIR spectra of each component from those of the composite, spectral insights for the entire sample are brought about.

Separation by Chemical Methods

A common method of chemically separating refinery or petrochemical soil components uses their different solubilities. Some components will preferentially partition into a polar solvent, while others will be soluble in nonpolar solvents. Solvents are classified as polar and nonpolar by their molecular structure. A polar solvent consists of dipoles. Dipoles are molecules in which the atoms are positioned so the centers of positive and negative electrical charges are at different locations in the molecule. Water is the most common polar solvent.

Traditional bench-top methods to evaluate organic refinery soils can be time consuming, and occasionally ineffective. Study of the materials obtained from these physical and chemical separations by using FTIR spectrometry not only reduced analysis time but provided insights that might not otherwise be accessible. The far-reaching effects of these insights may extend to the accuracy, efficiency, cost effectiveness, and environmental responsibility of future industrial chemical cleaning methodology. The following section contains several examples of how the use of FTIR augmented present industrial chemical cleaning methodology.

Examples of Deposit Removal Prediction by Using Component Class Correlation

Once functional groups present in a refinery or petrochemical soil sample are identified by FTIR spectrometry, information available in the literature about the properties of those groups may provide valuable insight to develop solvents for their removal.

Two samples, the first a powdered carbon material and the second black sooty metallic shavings, were analyzed for organic composition by using FTIR spectrometry. An examination of the spectral data for a xylene extraction residue of the first sample indicated that it was primarily a surfactant (see Figure 8). The class of surfactant appeared to be either a polyethylene glycol soya sterol (PEG25 soya sterol) or a nonsilicone defoamer.

When the residue of an acetone extraction was compared with that of a xylene extraction for the first sample, significant differences in the spectral data were observed.

Spectral library searches of selected peaks in the fingerprint region indicated that the residue of the acetone extract might contain at least two types of surfactant materials. One was a PEG-3 C12-14 alcohol. The other material was a cocoamphocarboxypropionic acid, cocobetaine or oleyl betaine material, lauroyl sarcosine, or a tridecylsulfate lauramphocarboxyglycinate sodium salt.

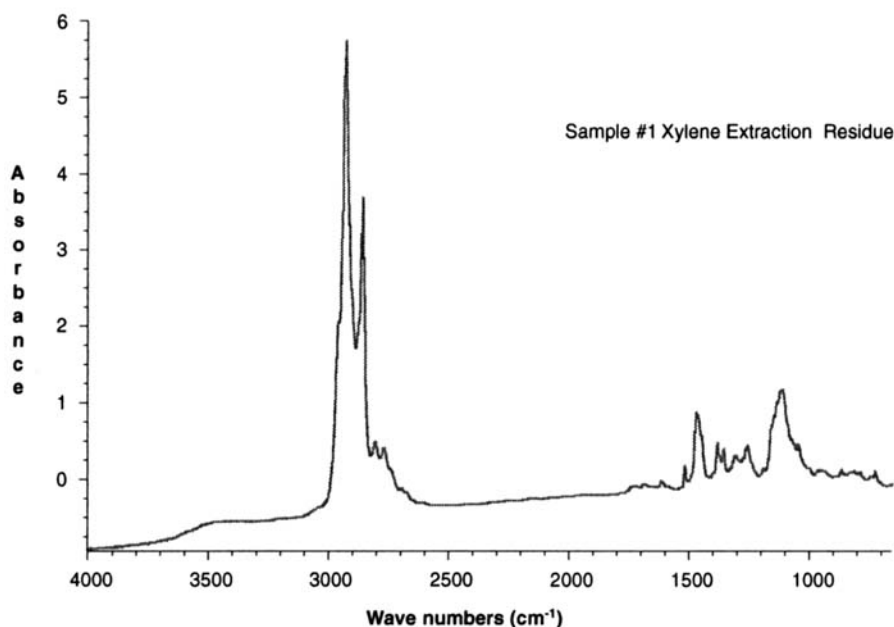


Figure 8. Spectral data of residue from xylene extraction of sample 1.

The second sample appeared to be black sooty metallic shavings. Following solvent extractions of this material with xylene and Freon, the solvents were evaporated, and the residues were analyzed by FTIR spectrometry. Because chlorinated solvents attack the epoxy that secures the zinc selenide crystal to the horizontal attenuated total reflectance (HATR) boat, Freon was air dried from the residue. The residue was resolvated in acetone for mounting purposes.

A spectral library search, restricted to the fingerprint region, strongly suggested the residue from each extraction was a defoamer. The class of defoamer was narrowed to a polyalkyl methacrylate copolymer in hydrocarbon oil. There were subtle differences between the residues from an acetone extraction and those of Freon and xylene. The appearance of peaks at 1852, 1774, and 1104 cm^{-1} strongly indicates a high-molecular-weight carboxylic anhydride as a component in the acetone extracted material. A spectral library search confirmed this by identifying the compound class as di- and tetra-substituted carboxylic anhydrides. These materials commonly occur in emulsifiers and lubricants.

Followup provided insight into the utility of the information afforded by FTIR analysis of the deposit. Until the deposit had been analyzed by FTIR spectrometry, neither the customer nor the field engineer could explain why cleaning effectiveness had varied in other thermal linear exchangers (TLEs) from those previously cleaned for the same customer. One idea was to develop a better understanding of the organic that might potentially be passed to the TLEs through the water treatment.

The FTIR analysis established that there were organics present in the form of surfactants and defoamer additives. These additives were believed to be the origin of the problem. Additional expense to the customers was between \$5,000.00 and \$12,000.00 for complete removal of the fouled deposits. However, they minimized the potential for the deposits to recur through process changes. The customers made a change in the level of water treatment chemicals that was used, the amount of organic amines was reduced, and a significant decrease in the fouling deposit was observed.

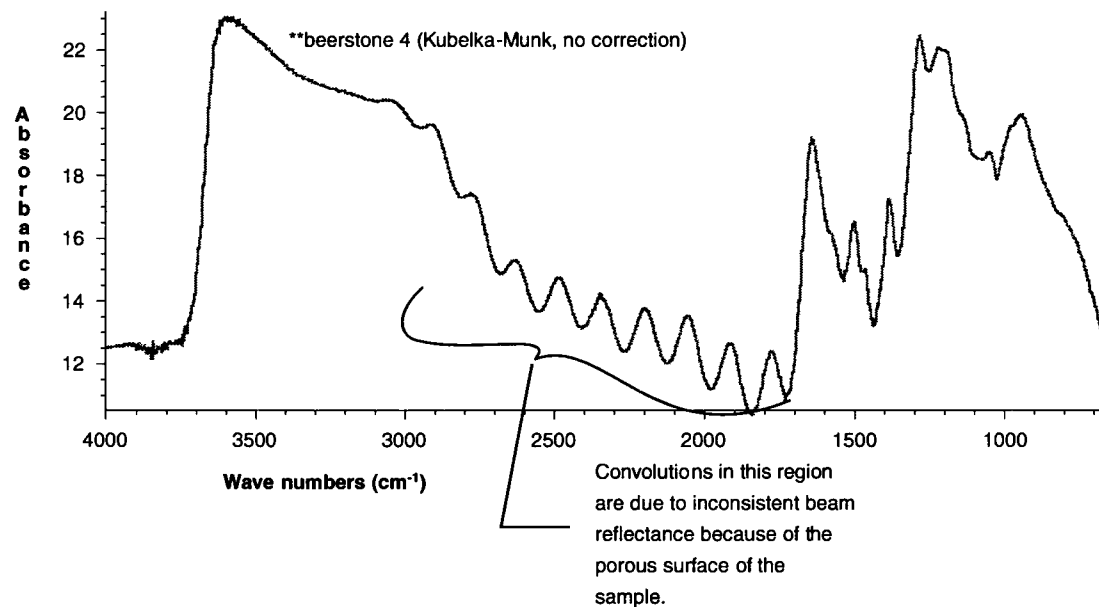


Figure 9. FTIR analysis of beerstone, using spectral reflectance.

The return on their investment will feasibly exceed the initial expense several fold, and they will likely achieve extended run length because of the thorough cleaning.

By identifying the organics and establishing that they were the cause of the difficulty in consistent cleaning, the customers were able to make process changes that reduced their problems and complemented the cleaning efforts. By providing this service, we advanced our value to the customers. The value in this case was our ability to identify the root cause of the problem, make the customers aware, and take appropriate preventive or corrective measures.

A sample of a hard, porous scale deposit, referred to as “beerstone,” was submitted for FTIR analysis. This sample came from a beer manufacturing plant, and it was assumed that a portion of the deposit was organic. A literature search confirmed the presence of organic entrained in a calcium oxalate matrix. Attempts to solubilize the material were unsuccessful.

Because the material could not be solubilized, a spectral reflectance accessory for the FTIR analysis was used in an attempt to identify organic functionalities. In brief, the spectral reflectance is based on a smooth surface that will allow the IR beam to pass through the surface coating of a metal or coupon, and be reflected back through the sample to the detector.

Although the deposit was not ideally suited for this method, useful information from the sample spectra was obtained (see Figure 9). The convolutions occurring in the region between 3000 and 1700 cm^{-1} are most probably due to the limitations of the spectral reflectance accessory with this porous sample. A better method for examining samples of this nature, although unavailable at the time this study was made, would be to use diffuse reflectance by powdering the material and mixing it with potassium bromide.

With the use of the major absorbing peaks around 3500 and between 1700 and 650 cm^{-1} , two potential classes of compounds were suggested. The organic portion of the deposit material appears to contain aliphatic ammonium carboxylic acid salts and tetra-aliphatic amides. A spectral library search on the augmented spectra (multiplied by a factor to increase peak intensity) suggested the compound class to be a urea-formaldehyde condensation product. Although the functional groups suggested by the absorbing peaks could be present in the process where this deposit was formed, it is likely that compounds containing these functionalities are not included in current spectral libraries.

The field engineer reported that the ethanol unit reboiler flash drums were hydroblasted instead of being chemically cleaned. This was because the deposit thickness was a thin film. However, three heat exchangers, related to the original piece of equipment, were chemically cleaned by using formic acid. This decision was based on the information provided from the FTIR analysis of the beerstone. The formic acid did a good job of cleaning the exchangers.

CONCLUSIONS

Cleaning procedures for refinery/petrochemical equipment will continue to emphasize less toxic chemicals, high-pressure water blasting (with water recovery), and considerations for the disposal of the waste materials. Continued use of analytical methods (such as FTIR) may reduce the time necessary to develop an appropriate cleaning sequence.

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6

DISPOSAL OF CHEMICAL CLEANING WASTES

Chemical cleaning wastes usually contain quantities of metals and other materials that exceed liquid discharge limits of the plants where the waste is generated. While the environmental revolution of the past few decades has increased the need for better disposal and waste minimization techniques, responsible cleaning vendors have been concerned with safe disposal for many years. The cleaning procedures may generate volumes of wastes that range from a few hundred gallons to several hundreds of thousands of gallons of waste fluids produced during cleaning of nuclear steam generators. Many methods have been devised to dispose of the wastes. We will review both mechanical and chemical methods of disposal. Since wastes containing chelating agents and complexing agents are more difficult to treat than wastes from cleaning treatments that use mineral acids, most of the literature is concerned with the more complex wastes. The procedures that were reviewed are divided into methods that are mostly mechanical, and those that are mostly chemical; however, all of the methods contain some mechanical and chemical procedures.

MECHANICAL METHODS

Incineration of chelant wastes has proven to be a very economical method of disposal for both EDTA and citric acid wastes. Development of safe incineration (now called thermal evaporation) techniques greatly enhanced the use of chelating agents at the expense of mineral acid formulations. Test burns of spent EDTA solutions were described by Sisson.¹ Following trial injections of spent EDTA chelants into the fire box of operating boilers, 65,000 gal (246,025 L) of spent EDTA chelant containing 19,000 ppm Fe and 320 ppm Cu were injected into a boiler operating at 255–260 MW. The burn lasted over 5 h at an injection rate of 180 gal/min (681 L/min). Over the time of the burn 1701 lb (771 kg) of iron and 9 lbs (4.1 kg) of copper left the stack (most of which was from the coal). The measured values of iron and copper were less than 1% of the threshold limit value (TLV) for those two metals. Wackenhuth² reported on the incineration of a citric acid waste in a coal-fired boiler. Over 18,000 gal (68,130 L) of an ammonium citrate waste containing 1560 lb (707 kg) of iron and 30 lb

(13.6 kg) of copper was successfully incinerated without adversely affecting the stack discharges. Hallaren³ summarized more than 10 years of successful incineration of wastes from chelant cleaning of utility boilers. Since the development of incineration as a technique for treating wastes, this method usually will be the least expensive procedure for disposal in localities where the technique is still legal.

Fluids resulting from cleaning the secondary side of nuclear steam generators were processed by reducing the volume by means of a submerged combustion evaporator,⁴ followed by solidifying the concentrated wastes. This process was used to treat 180,000 gal (681,300 L) of EDTA waste from the Oconee Station. An 85% volume reduction was achieved prior to solidification. Peters described the use of this process in more detail.⁵ Chemical cleaning solutions containing high concentrations of organic chelating wastes are difficult to reduce in volume by using existing technology. Current methods for evaporating low-level radioactive waste solutions often use high-maintenance evaporators that can be costly and inefficient. The heat transfer surfaces of these evaporators are easily fouled, and their maintenance requires a significant labor investment. To address the volume reduction of spent, low-level radioactive, chelating-based chemical cleaning solutions, a liquid volume reduction system (LVRS) was developed. The LVRS is based on submerged combustion evaporator technology that was modified for treatment of low-level radioactive liquid wastes. This system was developed in 1988 and was used to process 180,000 gal (681,300 L) of waste at Oconee Nuclear Station. An improved and modularized system was used at Arkansas Nuclear One to process approximately 170,000 gal (643,450 L) of chemical cleaning waste in early 1991. The LVRS provides nuclear utilities with an economically acceptable alternative for volume reducing nonstandard, difficult to process, low-level Class A radioactive solutions. After volume reduction, the concentrated waste solution is processed for burial. The procedure uses a waste solidification process that can solidify 40–48 gal (151–181 L) of waste in a standard 55-gal (208-L) drum, significantly reducing processing and disposal costs. The distillate from the evaporator undergoes a secondary processing step, if necessary, and is released after it meets all site discharge limits.

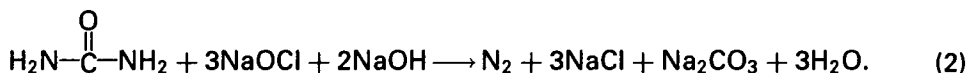
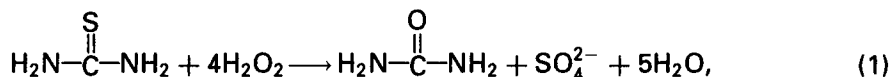
Snow⁶ has reviewed (53 references) a number of different methods for reducing the volume of nuclear steam generator wastes. Disposal methods that are mostly mechanical that were considered include direct solidification, thermal degradation, incineration, and evaporation. Direct solidification methods include addition of a cement binder and solidification with a vinyl ester binder. The latter method was used to solidify the NS-1 waste from the decontamination of Dresden-1 after partial evaporation to reduce the volume. Thermal degradation and incineration methods require a large amount of equipment to ensure destruction of the very stable EDTA molecule, which must be subjected to temperature $>200^{\circ}\text{C}$ (392°F) to cause rapid degradation.

CHEMICAL TREATMENT

Most of the chemical waste treatment methods use some form of precipitation technology to remove the heavy metals, which are the primary problem species. After precipitation, the slurry is allowed to settle, and the thickened solids are dewatered by using mechanical devices such as filter presses or centrifuges. Bell⁷ has reviewed treatment methods for treating many types of wastes. Spent mineral

acids are neutralized with alkaline-containing solutions. Each source of alkali (sodium hydroxide, lime, or sodium carbonate) have advantages and disadvantages. Copper-ammonia solutions can be treated by reducing the pH to about 7 to produce ammonium ions and to precipitate copper hydroxide.

Hydrochloric acid solutions may contain thiourea if this solvent is being used to remove copper and iron from a boiler. Since thiourea is a known animal carcinogen, treatment methods must include a step to reduce the concentration of this chemical. McConnell⁸⁻¹⁰ has developed an oxidation method for removing thiourea from acid solutions. Alkaline solutions can be oxidized to carbon dioxide and nitrogen in a two-step procedure.



Many metals can be precipitated from chelant wastes by means of chemical treatments. Rogoshewski¹¹ tested the use of lime and dilution of cleaning wastes with air preheater washing wastes. If the waste from the treatment of the boiler (ammoniated citrate or hydroxyacetic acid/formic acid) were diluted by about 7/1, lime treatment was effective as a method of reducing heavy metal concentration to <1 ppm. Uhr¹² conducted a literature survey of disposal methods for citrate and gluconate containing waste streams from chemical cleaning and metal treating processes. His paper included the functions of citrate and gluconate in formulations, other additives possibly present, and interference caused by citrates and gluconates in alkaline precipitation of heavy metals. Citrate is recommended as easiest to treat for disposal by oxidation with ozone, peroxide, persulfate, or hypochlorite, followed by addition of lime and NaOH to raise pH and precipitate citrate as the calcium salt. Additives discussed include ammonia, fluorides, reducing agents, surfactants, and inhibitors. Although gluconate may be precipitated with lime at pH 12 or destroyed by boiling with about 300 ppm ferric ion in NaOH solutions, neither technique reduces gluconate concentration below guidelines. Chemistry of chelation, buffering, precipitation, and oxidation of citrates and gluconates is described.

Treatment of more concentrated chelant wastes requires the use of a more aggressive chemistry. Kennedy¹³ demonstrated that iron and copper could be removed from EDTA by a combination of lime, NaOH, and diethyldithiocarbamate. By this process, >99.9% of the iron and copper was removed. However, only 82% of the nickel was precipitated. Samuelson¹⁴ described the use of this technology to treat several waste streams from operational cleaning of utility power boilers.

The problems of treating wastes containing high concentrations of nickel were addressed by Hoy.¹⁵ This metal can be removed by heating the waste to temperatures of about 180°F (82°C) in the presence of a thiocarbamate and calcium. After being heated to 180°F (82°C), then cooled to room temperature, Ni concentrations in EDTA fell from 35 ppm to 2 ppm in 120 h. Similar chemical processes were used by Radtke¹⁶ to treat over 200,000 gal (757,000 L) of EDTA waste from the cleaning of a nuclear steam generator at the Byron station. This waste contained high concentrations of iron and nickel and small amounts of copper and chromium. Lime and a proprietary organic sulfur precipitator (OSP) and a mild (150°F, or 65°C) thermal treatment was

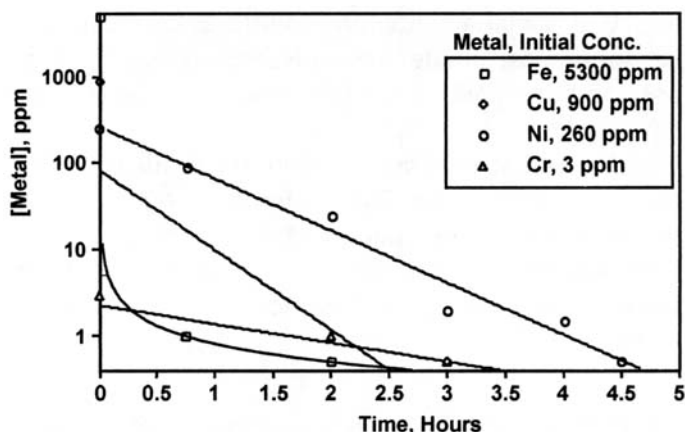


Figure 1. Precipitation of metals form EDTA waste with lime and organic sulfur precipitant at a temperature of 150°F (65°C) and a pH of 10.8.

used to accomplish adequate metals reduction. Figure 1 shows the metal reduction rates of iron, copper, nickel, and chromium form a real boiler waste used during the development of the process used to treat the nuclear wastes. The solution was heated to 150°F (65°C) in the presence of lime, NaOH, and OSP. Total metal removal was accomplished in less than 10 h. The schematic of the mechanical procedures used at Byron is seen as Figure 2. The effluent was released to the plant’s outfall. All metal values were <1 ppm prior to discharge.

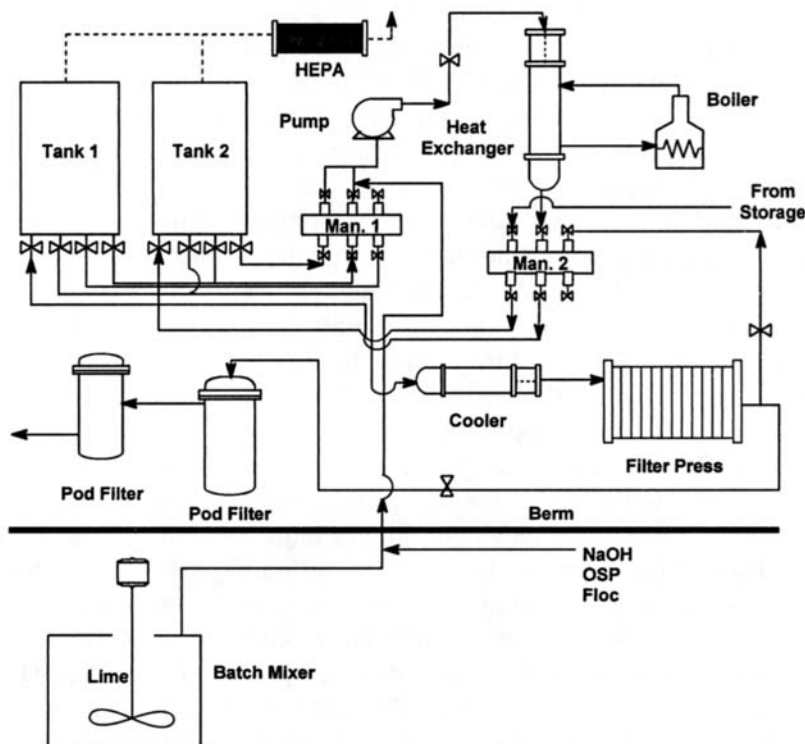
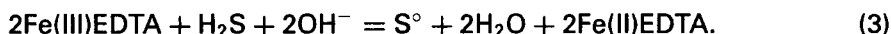


Figure 2. Schematic of waste treatment at the Byron One nuclear plant.

A number of other chemical treatments for steam generator cleaning wastes containing EDTA were reviewed by Snow.⁶ Processes for chemically destroying the EDTA waste that were considered include oxidation, ozonation, wet-air oxidation, and photodegradation. The most promising technique was a combination of oxidation and photolysis with UV light. Details of UV/peroxide treatment of steam generator wastes were presented by Karell.¹⁷ This author concluded that UV/peroxide treatments would not be cost effective for large volumes of steam generator wastes.

Additional treatment methods have been claimed in the patent literature for removing metals from EDTA-containing wastes. Frost¹⁸ claimed a process that included the addition of a sulfide, separation of metal sulfides, and then oxidation by sodium nitrite at 575°F (302°C). Complete removal of metals, including chromium, is claimed. A process for removing heavy metals from solutions containing chelating agents was proposed by Guess.¹⁹ This process includes the addition of ferrous ions followed by addition of the sodium dithionite to precipitate the metals. A reverse osmosis technique was developed by Terao²⁰ for treating boiler cleaning wastes containing citric acid.

A very different approach to disposal of chelated iron boiler wastes made use of these materials to oxidize hydrogen sulfide at the Geysers Power Plant²¹ in California. The spent EDTA-iron waste was used to oxidize the sulfide gasses produced with the geothermal steam. The chemical reaction is as follows:



The use of the waste iron-EDTA solution is an important idea that has also been considered in the past. EDTA-containing boiler wastes have been spread on dormant alfalfa.²² The farm plots treated with diluted boiler wastes produced more crop than the untreated plots. This probably is due to the ammonia and iron contained in the boiler cleaning wastes. More attempts to reuse the valuable metals and “chelated micronutrients” should be investigated.

CHEMICAL AND BIOCHEMICAL DEGRADATION

Most of the previous discussion was concerned with removing the metals from cleaning wastes. The organic portion of the waste also may require treatment. Disposal of EDTA is a particular problem since it is not very biodegradable. EDTA and other polyaminopolycarboxylic acid chelating agents undergo hydrolysis and other degradation reactions when heated to moderately high temperatures. Venesky²³ showed that EDTA was not stable above 200°C (392°F) and postulated that the reactions were initiated by dissolved oxygen. Martell²⁴ studied NTA and EDTA in aqueous solution and showed that EDTA is cleaved at the C—N bond at 260°C (554°F), but NTA was much more stable and did not decarboxylate rapidly until 290°C.

Motekaitis²⁵ determined the kinetics of hydrolysis and ammonolysis of EDTA at temperatures of interest for chemical cleaning activities. The rate increases with decreasing pH in the presence of ammonia. The rates are high enough at temperatures above 160°C (320°F) to affect the commercial use of ammonium EDTA. The molecule is cleaved at the C—N and C—C bonds. EDTA is rapidly oxidized by ferric ions. Motekaitis²⁶ also determined that ferric EDTA would oxidize other EDTA molecules rapidly at temperatures as low as 125°C (257°F). The major reaction cuts off carboxylate groups in a sequential fashion. NTA is oxidized more slowly than EDTA.

The oxidation of EDTA, NTA, and DTPA by various peroxo compounds has been the subject of intense investigation. Snow⁶ reviewed various oxidation techniques for degrading EDTA. The most effective methods are oxidation by ozone or hydrogen peroxide and UV light. Karell¹⁷ studied ways for degrading EDTA in the presence of dissolved ferric iron and concluded that the use of peroxide and UV light at 254 nm was the most effective method. However, he concluded that this method was too expensive to use to degrade nuclear cleaning wastes because the degradation products also are chelating agents and could stabilize radioactive metals.

Iron dissolved in EDTA can significantly influence the degradation process by means of Fenton chemistry.²⁷ In the Fenton reaction, a ferrous chelate is oxidized to a ferric chelate by hydrogen peroxide and liberates a hydroxyl radical that causes further oxidation of chelate molecules in solution. See Equation (4):



Chen^{27,28} has determined that the sequence of degradation of chelating agents by peroxide by means of the Fenton reaction is $\text{NTA} < \text{EDTA} < \text{HEDTA}$. The chelating agent DTPA is the most chemically stable material in the presence of peroxide and iron. The major reaction products are iminodiacetic acid (IDA), hydroxyethyliminodiacetic acid (HEIDA), and glycine. All of these materials are still capable of complexing many metals, albeit not as strongly as EDTA.

An alternate approach is to develop biodegradable chelants capable of being used in cleaning formulations or developing microorganisms capable of feeding on EDTA. Lauff^{29,30} found that *Agrobacterium* is capable of degrading EDTA or PDTA complexes in wastewater. Optimal Fe^{3+} EDTA degradation occurred below pH 7. This author also described a pure culture of *Agrobacterium* sp., which was isolated from a waste treatment facility. The isolate grew on ferric EDTA as the sole carbon source. The degradation produced carbon dioxide, ammonia and an unidentified metabolite. The rate of degradation was 24 mM/day. In a similar vein, Bunch³¹ studied settled sewage sludge, which was used to inoculate biological oxygen demand (BOD) dilution water. After 7 days, the test solutions were tested for the chelating agents. NTA and HEIDA lost their chelation ability, while EDTA, DTPA, HEDTA, and cyclohexylethylenediaminetetraacetic acid (CYDTA) were unchanged. It was concluded that chelants with single nitrogen are biodegradable, but those with two nitrogen atoms are not biodegradable.

Gousetis³² claimed uses of biodegradable chelants. Stability constants were determined for the isoserinediacetic acid chelating agent and the uses of it in laundering for stabilizing bleach and as a detergent builder were exemplified. Toxicity was somewhat greater than EDTA or NTA, and biodegradability was at least as good. A continuous process for manufacture of trisodium salt of isoserine-*N*, *N*-diacetic acid as an additive for cleaners and detergents is described by Widder.³³ Baur³⁴ claims the preparation of additional isoserine derivatives and their uses as complexing agents for heavy metals and as stabilizers for bleach in detergent formulations. Wilson³⁵ has claimed the use of ethylenediaminedisuccinic acid (EDDSA) types of chelating agents in a number of applications. There are also claims that this material is biodegradable.

Means³⁶ described the degradation of NTA, EDTA, DTPA, and HEDTA in soil. Degradation of NTA, EDTA, and DTPA increased in the presence of nutrients and decreased with decreasing oxidation potential. In the short term, the order of rate

of degradation was DTPA > EDTA > NTA, but in the long term (180 days), NTA ~ DTPA > EDTA. Photodegradation was greater for DTPA than for EDTA or NTA. Degradation of all three chelants was not rapid enough to preclude concern about their release into the environment. HEIDA is much more biodegradable than EDTA and is claimed as an ingredient in surface treating formulations.³⁷

CONCLUSIONS

The continued use of chemicals to descale industrial equipment requires waste minimization and waste disposal techniques that are cost effective with other cleaning methods such as high-pressure water and on-stream cleaning. This author believes that the development of safe, biodegradable cleaning agents is the number-one challenge of the cleaning industry.

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7

CLEANING NUCLEAR EQUIPMENT

Processes to clean nuclear power-generating equipment can be considered specialized applications of the iron oxide and copper dissolution methods considered earlier in this book. However, because of the radioactivity usually present in deposits that foul nuclear generating equipment, specialized procedures have been developed to clean some types of nuclear equipment. Three different types of processes are conducted: (1) chemical treatments are used to decontaminate parts of the units to allow maintenance or before decommissioning the plant (these are health physics issues); (2) the secondary sides of PWR steam generators are being cleaned to remove crud and to slow the formation of “dents” that restrict flow in the steam generator and could actually crush the tubes (this is described in more detail later in this chapter); (3) various service water-containing systems have been cleaned for all of the reasons described in Chapter 1.

DECONTAMINATION

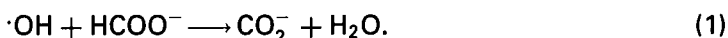
The buildup of radioactive contamination on out-of-core surfaces leads to occupational radiation exposure when these surfaces are manually maintained or serviced. Decontamination is the process by which a portion of the radioactive species is removed to allow servicing of the unit or if required prior to unit decommissioning. Physical techniques, such as abrasive cleaning, have very limited use in system decontamination since they are limited to surfaces that are relatively accessible. Chemical methods can be applied to an entire loop or an entire reactor unit. Solvents to remove radioactivity from stainless steel or other similar alloys have included stages of alkaline permanganate (AP) with ammonium citrate (AC), ammonium citrate/ammonium oxalate (CITROX), and regeneration of weak chelate solutions with the CANDECON and CANDEREM processes. In addition, the powerful reducing agents contained in the LOMI technologies will be described later in this chapter.

A symposium¹ held at Ohio State University (OSU) in 1975 was sponsored by the Electric Power Research Institute (EPRI), the American Society of Mechanical Engineers (ASME), and OSU to summarize the state of the art at that time. Significant technologies described included the use of chelants such as EDTA and citric acid as

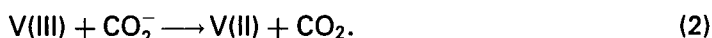
well as regenerative processes such as CANDECON. Many of these processes are now being used to decontaminate various parts of operating nuclear plants. Wood² reviewed progress up to 1991 and more recently³ from 1991 to 1994. According to this author, there have been more than 40 decontamination procedures performed. The technologies used include all of the methods described above. Issues of concern include waste processing and corrosion, as well as the size of the decontamination factors (DF-reduction in radioactivity) achieved. The following sections will describe the development of some of the major processes now in commercial use.

The AP/CITROX process uses alternating oxidizing stages of 12% alkaline permanganate with reducing stages of 6% ammonium citrate/ammonium oxalate and can produce DF values of 10–100. While these processes have been performed since 1970,⁴ these chemicals produce very large volumes of waste and are very aggressive and corrosive. The LOMI technologies were developed to provide less aggressive reagents that would still reduce radioactivity.

Loose crud found on PWR primary side surfaces generally is composed of variations of nickel ferrite (NiFe_2O_4), while deposits on boiling water reactor (BWR) surfaces include iron oxides such as Fe_2O_3 or FeOOH . Fe_3O_4 containing deposits also may be present. The LOMI reagents provide reducing environments that causes some change in the oxidation state of the iron ions. Bradbury⁵ traces the development of some LOMI reagents. He found that the rates of oxide dissolution were greatest for one-electron reducing agents such as V^{2+} , Cr^{2+} , HSCH_2COOH , and $\text{Na}_2\text{S}_2\text{O}_4$. He rationalizes this observation by concluding that the reduction process of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ requires only one electron per site. The most effective reducing agents were V(II) bipyridyl and V(II) picolinate. The bipyridyl reagent was not stable in the presence of the ionizing radiation present in the reactor. In the presence of excess formic acid, the V(II) ion can be protected from oxidation by the hydroxyl radicals produced from water radiolysis:



The carbonyl ion will reduce any V(III) produced from oxidation by the hydroxyl radical or the ferric iron in the deposit:



Low concentrations (0.1%) of the vanadous picolinate (V(pic)_3^-) are dissolved in formic acid (pH about 4). These solutions have been utilized to remove all of the deposited oxides presently found in BWR systems. To utilize these reagents, the circuit is filled with a degassed (the reagent is sensitive to air) solution of picolinic acid, an alkali to bring the pH to about 4, and is circulated at about 80°C. A concentrated vanadous formate solution is injected. The amount of vanadium should be equal (molar amount) to the iron in the deposit. After circulation for a time sufficient to achieve decontamination, the entire solvent is diverted through a mixed-bed ion-exchange bed to remove all of the reagents. The Bradbury report includes detailed investigations of the vanadium reagents and described uses of other potential LOMI reagents, including Cr(II)bipyridyl and several based on EDTA.

A much more concentrated solution has been used to remove uranium dioxide (UO_2) contaminants from the Three-Mile Island-2 reactor.⁶ The solvent contained oxalic acid, sodium gluconate, gluconic acid, 8-hydroxyquinoline, and hydrogen peroxide, and it is called the “OPG” solvent. A modified OPG solvent (pH 4.5 and 60°C)

was used to decontaminate a fueling machine in a CANDU reactor.⁷ Decontamination factors as high as 35 were achieved by using two stages of the modified solvent. Since iron-containing sludge of surfaces catalyze the decomposition of hydrogen peroxide, the process is most effective when these surfaces are at a minimum.

Dilute solutions of organic acids that are regenerated by using a cation exchange resin form the basis for the CANDECON⁸ process. The organic acids (citric and oxalic acids) are added to the cooling water at about 0.1% by weight, and the solution is then passed through a cation exchange resin. This resin removes the metal ions and regenerates the acid in the solvent. Several studies have been performed by Speranzini⁹⁻¹¹ on the corrosivity and decontamination effectiveness of mixtures of EDTA, citric acid, and oxalic acid. Mixtures of EDTA with citric acid were more effective than citric acid or citric/oxalic acids as solvents for BWR oxides. Oxalic acid improved the decontamination in some situations but also contributed to increase in the intergranular attack (IGA) of sensitized series 304 stainless steel. In these studies, oxalic acid was removed from the CANDECON solutions and EDTA was added. The modified solution system was named CANDEREM¹² and was used with stages of alkaline permanganate to decontaminate steam generator channel heads at Beaver Valley-I station. Decon factors of 4.8 to 6.5 were achieved with this process use of dilute chemical decontamination processes was described by Murray.¹³ These processes use solutions (about 0.1%) of organic acids and chelating agents¹⁴ that are circulated for 2–48 h and then are disposed of by using ion exchange resins. These methods must be used more frequently than more concentrated solvents; however, decon factors as high as 50 can be obtained by using these reagents.

Much of the technology developed for decontaminating worldwide nuclear plant components was reviewed¹⁵ during a joint meeting of the American Nuclear Society and the Canadian Nuclear Association held in 1982. This conference addressed mechanical as well as chemical decon methods. Unusual technology described included the use of a nitric acid/permanganate stage for PWR decontamination (Peck, paper 3-5), a foam cleaning method (Harris, paper 4-37), as well as a whole session on the experience decontaminating TMI-2.

DRESDEN-1

Dresden-1 was one of the first commercial nuclear reactors. Put into service in July 1960, this 200-mWe BWR, located outside Morris, IL, was owned and operated by Commonwealth Edison. The reactor and turbine set were both designed and manufactured by General Electric. The unit was taken out of service in October 1978.

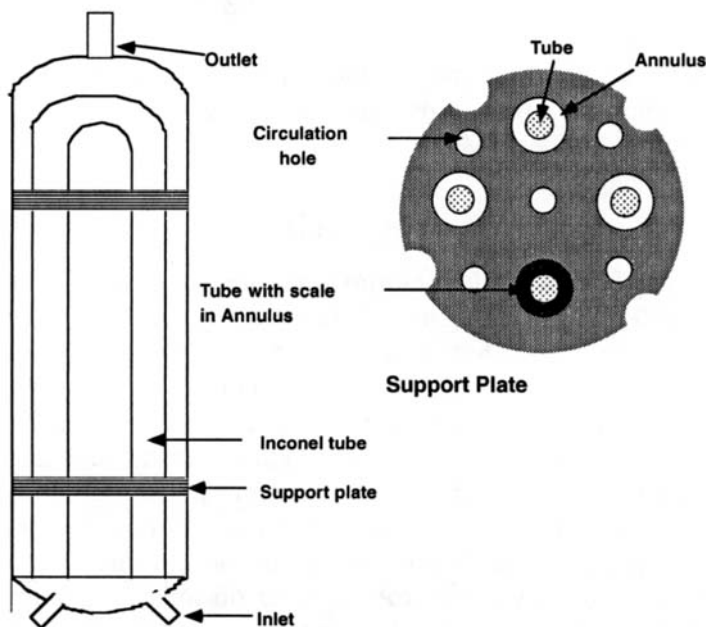
A low-pH mixed chelant system containing proprietary corrosion inhibitor and additives was selected to perform the cleaning task. Extensive metallurgical verification, engineering reviews, and corrosion tests were performed and double checked to qualify the process. The process called for the cleaning solution to be applied at 200°F (93°C) and to be circulated throughout the primary circuitry, reactor vessel, steam drum, secondary generators, and so on for a minimum of 100 h and a maximum of 200 h. Laboratory tests indicated that decontamination factors as high as 1000 could be achieved.^{16,17} During the actual cleaning, comprehensive chemical and isotopic analyses monitored the progress of the cleaning and provided data to determine if termination criteria had been met.

An evaluation of the results showed that the solvent system performed as designed and the goals of the decontamination had been achieved.

CLEANING STEAM GENERATORS

Steam generators of PWR nuclear reactors are very large heat exchangers in which the water from the core produces steam that is used to drive the turbines of the power plant. The water (and thus the deposits) on the shell side (see Figure 1) of the steam generators should be nonradioactive, but because of leaks, low levels of radioactivity may be present. The tubes usually are constructed of a nickel-chromium-iron alloy while the shell and the plates that support the tubes are constructed from a carbon steel alloy (in early units). In units built after corrosion was recognized to be a problem, the plates were constructed of ferritic stainless steel. The tubes may be arranged as once-through or in a U-tube design. The deposits that form in the generators usually contain magnetite as well as varying amounts of copper. The deposits may form a sludge that collects on the support plates as well as in a pile at the bottom of the generator. A more insidious "linear fast-grown magnetite" also can form in the annulus between the tubes and the support plates. This material can "dent" the tubes as it grows and can crack the support plates and may cause the generator to lose capacity and thus power rating. Because access to the shell side is limited and flow is difficult to achieve, cleaning of steam generators is one of the greatest challenges the chemical cleaning industry faces.

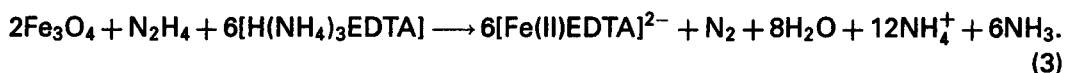
Since much of the magnetite deposit is not in electrical contact with a reducible substrate, an external reducing agent usually is a part of the solvent mixture. Pitzer¹⁸ proposed a mixture of ammonium EDTA with 0.1–0.5 M of hydrazine, used at



Typical "U" Tube PWR Steam Generator

Figure 1. Schematic of PWR steam generator and support plate.

pH 6.5–9.5. This solvent could dissolve most of magnetite pellets as well as a mixed (iron, nickel, cobalt, chromium) oxide scale from a reactor. The treatment temperature usually was about 95°C. Pocock¹⁹ also recognized the need for a reducing stage when he tested a number of different solvents for dissolving iron oxide, nickel oxide, and chromium oxide. Various EDTA and citric acid formulations were used with reducing agents including ascorbic acid, glucose, thioglycolic acid, and hydrazine. The solvent also contained a commercial corrosion inhibitor. Based on static and dynamic tests, the most effective solvent was ammonium EDTA with 1% hydrazine at a pH of 7. This solvent was very effective in dissolving the iron oxide, somewhat effective for dissolving the nickel, and not very promising for the chromium oxides. The corrosion of the tube and support plate material was of significant concern, and this area of concern dominates many of the subsequent studies of solvents for steam generator cleaning processes. The reaction is



Pettit²⁰ described tests to develop a solvent for PWR deposits, especially to remove the denting deposits. A total of 14 solvent combinations were tested on a synthetic sludge that contained iron oxide, copper oxide, nickel oxide, chromium oxide, and various minor contaminants. The most promising solvents contained EDTA and citric acid or citric acid and ascorbic acid, as well as corrosion inhibitors (such as diethylthiourea). It was also determined that an oxidative copper stage would be required at some place in the process. Frost,²¹ Blakrishnan,²² and McSweeney²³ developed a process that uses a copper-removal “pre-stage” consisting of ammonia and air to remove the bulk of the copper. Iron-removal stages follow. These use ammonium EDTA containing citric acid, hydrazine, and a corrosion inhibitor at 90–95°C. A final copper stage using ammonia and air completed the process. The procedure was used to remove 500 kg of magnetite, 200 kg of copper, and various other deposits from the Nuclear Power Demonstration Nuclear Generating Station of Ontario Hydro in Canada.

In 1977, the Electric Power Research Institute, in conjunction with the Steam Generators Owners Group (SGOG), sponsored work to develop a generic, nonproprietary²⁴ system for cleaning steam generators. This effort produced the EPRI/SGOG solvent system, as well as a bookshelf of reports. We will review the most significant reports. Welty²⁵ described the overall progress at NACE International and American Power Conference meetings in 1982. A total of 48 iron oxide solvents were tested to determine solvency as well as corrosivity toward A-36 carbon steel electrodes. The solvents included EDTA, HEDTA, NTA, DTPA, and citric acid salts (usually ammonium). Reducing agents included ascorbic acid and hydrazine. Two solvents, EDTA and hydrazine at pH 6.0, and EDTA, citric acid, and hydrazine, also at pH 6.0, were tested in a mock-Up apparatus containing several different metals. The inhibitor was the nonproprietary CCI-801 material (more discussion later on this subject). The solvent without citric acid produced significantly less corrosion than the other material and was chosen for further development.

Two copper-solvent approaches were tested: 10% ammonia with an air sparger or EDTA/ammonia/ethylenediamine/H₂O₂. The latter system produced much less corrosion to exposed steel than the ammonia/air mixture, while being able to remove large amounts of copper. The solvent system finally chosen was (1) copper stage;

5% EDTA, 2% H₂O₂, pH 7.0 w/NH₃, pH 10 with EDA; (2) Fe stage; 10% EDTA, 1% N₂H₄, 0.5% CCI-801, pH 7.0/NH₃. With the exception of the amount and type of inhibitor used, the iron solvent is identical to the formulation recommended by Pocock¹⁹ in 1971.

The development and testing of a nonproprietary corrosion inhibitor for the EPRI solvent was a very important part of the solvent development process. Hausler²⁴ tested more than 200 compounds from 15 different chemical categories in a solution of 10% EDTA, 1% N₂H₄, pH 7.0 with NH₃. The solution also contained 17.5 g/L Fe₃O₄ (to simulate dissolving scale). The chemical categories included thioureas, a number of categories of aliphatic and aromatic amines, acetylenic alcohols, alkyl pyridines, and pyrimidines. Only sulfur-containing compounds such as dibutylthiourea, TIA (tetraimidazoline derivative), and alkylpyridines gave more than 90% protection in the initial screen. The sulfur compounds and the alkylpyridines were rejected because of solubility problems. A new class of compounds, imino-amido condensation products (CCI-801) containing thioether linkages, were synthesized and found to give >90% protection at 160°F (71°C) and 250°F (121°C). The final experimental formulation was made. TIA was rejected because it would not protect SA-533-A steel at 250°F (121°C). The experimental formulation was then used in pilot-size pot boilers and model boilers with EDTA/hydrazine to clean sludge and remove magnetite from simulated crevices.²⁵ Some concern was expressed about the sulfur content (~1.25%) in Hausler's experimental formulation, since there were fears that residual sulfur might cause cracking of the Alloy 600 tubes found in nuclear steam generators.

Several reports summarized and reviewed the EPRI/SGOG²⁶ development effort. Jevac²⁷ reviewed the work on developing the iron sludge solvent, including the tests to determine if citric acid was a desirable additive, proper concentration of hydrazine, and optimum pH. Three types of copper solvents were reviewed: EDTA/sodium nitrite; ammonia/air; and EDTA/peroxide/EDA. The development of analytical and monitoring techniques was addressed.

A report by Cleary²⁸ reviewed data as well as 24 reports written by other authors. The generic process described in Table 1 was judged to be generally applicable for use on Westinghouse steam generators.

In a very concise review, Welty²⁵ described the entire research and development process and results that lead to the EPRI/SGOG procedures. Since these have been discussed at length above, the discussion will not be repeated. Two areas of concern, the effect of residual sulfur from CCI-801 and galvanic corrosion to various weldments, have been the subject of continued work.

TABLE 1
EPRI/SGOG Processes

Process Step	Chemistry	Temperature
Iron sludge removal	10% EDTA, 1% N ₂ H ₄ , 0.5% CCI-801, pH 7.0/NH ₃	195°F ± 5°F (91°C ± 2°C)
Copper sludge removal	5% EDTA, 2% H ₂ O ₂ , pH 7.0/NH ₃ , pH 10/EDA	<100°F (38°C)
Crevice cleaning solvent	20% EDTA, 1% CCI-801, pH 6.0/NH ₃	250°F ± 5°F (121°C ± 2°C)
Passivation solution	NH ₃ to pH 10.2, 300 ppm N ₂ H ₄	200°F (93°C)

A review of the various corrosion issues was presented by Leedy.²⁹ The discussion included the free corrosion rates on various metals (controlled successfully) as well as the galvanic corrosion of weldments. The author concluded that the attack on the weldments would not be excessive in the geometries expected in steam generators (SGs). Processes based on the EPRI/SGOG development effort have been used to clean SGs at Three-Mile Island-1,³⁰ Byron 1, Sequoyia 1 and 2, Surrey 1 and 2, Callaway and Kori (Korea), Duke Oconee, and Ontario Hydro Pickering.

A number of alternative or foreign processes have been developed and used to clean SGs outside North America. Oliver³¹ presented a two-stage process that was used to remove 6300 lb (2857 kg) of iron and 960 lb (435 kg) of copper from a PWR in Spain. The iron solvent was described as an "acetic acid base at high pH." It was applied at 360–430°F (182–221°C) as the unit came off of the line, with an exposure time of about 2 h. The copper solvent was described as "ammonia base, high pH, air." It was applied at <140°F (60°C). The authors claim that the corrosion rates were within accepted parameters.

Saurin³² and Fiquet³³ described the development and use of a citric acid/gluconic acid process developed by EDF in France. A gluconic acid (7.5%), citric acid (4%) mixture at a pH of 3.3 (ammonia) and inhibited with "P6" were applied at 85°C (185°F) to remove the iron oxide deposits. The same solution (after the pH was raised to 10 with ammonia) was used to oxidize copper. Air provided the oxidizing power. A final "passivating and inhibitor removal" stage consisted of citric acid, MEA, and butynediol (pH 4). Operational experiences at three French and Belgian nuclear plants were detailed. The solvents removed 280–1500 kg of iron oxide and 2–38 kg of copper from the generators. Additional work by Noel³⁴ at EDF was conducted to determine the extent of degradation reactions on the chemicals used in descaling operations. The study showed that the organic compounds used have no interaction with the resins during radioactive waste storage and do not present a leaching risk.

Hur³⁵ described testing to qualify the EPRI/SGOG for use at temperatures up to 125°C (250°F). The process was used in a test reactor and claimed successful removal of sludge. The benefits are shorter cleaning times and more effective sludge removal as compared with the 93°C (200°F) process. Roofthoof³⁶ described several techniques that have been used in Belgium to clean the secondary sides of steam generators. These include the EDF and EPRI/SGOG processes described above, as well as the Siemens process, which is based on modified EDTA chemistry. The iron solvent is used at concentrations between 1% and 6% EDTA, while the copper process uses EDTA, EDA, and air at an alkaline pH value. General procedures on different reactors were also described. None of them were completely successful for cleaning the crevices. The Siemens process was judged to be easier to apply because it was performed during the shutdown time of the plant and took a shorter time to apply than the other procedures.

Additional process improvements were suggested by McSweeney.³⁷ A parametric study of the peroxide degradation reaction,



was conducted. Peroxide degradation and foaming was related to the amount of ammonia and iron, and the temperature of the process. The author recommended

that EDA be added to diammonium EDTA to raise the pH to 9.5, the iron concentration be limited to <100 ppm, and the temperature be at <35°C.

Several mechanical processes have been described. Varrin³⁸ detailed the development and use of a water jet nozzle array for removal of adherent scale from the secondary side tube surfaces. The array can deliver water at pressures up to 4500 psi (31.02 MPa) and was tested at Indian Point 2 nuclear plant. A mixing process was claimed by Buford.³⁹ The system includes pumps, educators, and gas injection to improve mixing and agitation of the SG cleaning solvents.

Esposito⁴⁰ described a chemical/mechanical procedure called pressure pulse cleaning, which uses the EPRI/SOGG chemistry. The generator is filled with the cleaning chemicals, while high-pressure nitrogen is pulsed at regular intervals into the bottom of the generators. The sudden displacement enhances fluid mixing and dislodges some crevice deposits. The procedures were demonstrated at the Westinghouse Axial Test Facility and in operational cleanings at Sequoya I and II.

CLEANING AUXILIARY EQUIPMENT IN A NUCLEAR PLANT

The largest known service water system chemical cleaning was performed at the Gulf States Utilities Company, River Bend Station. Brice⁴¹ described the process, which consisted of an iron oxide dissolution stage (IRS), alkaline stage (AS), copper-removal stage (CRS), and a layup stage (LUS). The first iron stage used sodium HEDTA at an acidic pH with a commercial corrosion inhibitor. This stage lasted about 100 h. The AS consisted of TSP and a surfactant. The CRS used an alkaline chelating agent and a liquid oxidizing agent. The final layup stage used high-pH water containing an oxygen scavenger. The cleaning removed approximately 17,000 lb (7711 kg) of Fe and 700 lb (317.5 kg) of Cu.

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8

SPECIAL TECHNIQUES

While chemical cleaning solvents usually are applied by pumping solvents through process equipment or power boilers, several other methods of applying them have been used. These include foams, "vapor phase" solvents, and special methods for cleaning pipelines. Because of the literature available, only foam cleaning and pipeline cleaning procedures will be reviewed.

FOAM CLEANING

Reactive chemical foams were used for many years to clean equipment that cannot (or should not) stand the weight of a liquid fill, or if it is not economical to fill the equipment with liquid. Industrial process equipment that has been successfully cleaned with foam include utility surface condensers, towers, tanks, and utility power turbines. A short theory section is presented.

Foam Technology—Theory

Foams are coarse dispersions of gas in a relatively small amount of liquid.¹ Foams cannot form from pure liquid. The thermodynamic equation is

$$DF = sDA - pdV, \quad (1)$$

where DF is the change in Helmholtz free energy at constant T , s is the surface tension of the liquid, A is its surface area, p is the pressure, and V is the volume of the gas. Equation (1) applied to a foam shows that a decrease in free energy results from the loss of area and expansion of the gas, both of which come about by coalescence of the bubbles; hence, a foam composed of a pure liquid is thermodynamically unstable. The third component necessary for a stable foam is usually a solute in the liquid, but can also be a finely divided solid, a liquid/crystal, or an insoluble monolayer. The stabilizer must be surface active (migrate to the interface) and be positively adsorbed. The work necessary to desorb the stabilizer is added to Equation (1) to give

$$DF = sDA - pdV + W(\text{desorption}). \quad (2)$$

This term may make the whole equation positive (thermodynamic stability); however, even when the foam is not completely stable (as is the case with most foams), the work of desorption reduces the decay rate of the foam.

The elasticity of the surface layer as well as the “Marangoni effect”² (explained below) help to stabilize the foam. The draining of a liquid, including the motion of a surface that carries an adsorbed layer, creates fresh surfaces of higher surface tension (surfactants usually lower the surface tension), a nonequilibrium temporary condition. The local difference of surface tension is removed by the motion of the surface from regions of lower to higher surface tension. This is called the Marangoni flow, and it opposes the movement of drainage and acts as a stabilizing factor to restore the thickness of the lamella layer. Thus, agents that create large differences in surface tension or increase the elasticity of the lamella will lead to greater foam stability. Although a surfactant lowers the surface tension of the liquid, lamella may lack cohesion. A second agent (“foam stabilizer”) may be necessary to increase cohesion. Chemicals that increase the surface film viscosity will act as stabilizers.

The rate of drainage frequently can be described by an exponential equation:

$$V = V_0 \exp(-kt), \quad (3)$$

where V is the amount of liquid that drains in time t , and V_0 is the total amount of liquid in the foam. This equation was used to describe drainage rates from many different types of slow-draining foams. The constant k is equivalent to a first-order rate coefficient.

Materials that inhibit or “break” foam should have a low surface tension, be destructive to the cohesion of the film, be insoluble in the aqueous phase, and have a low volatility. The polydimethylsiloxanes³ do all of these things and are the most universal antifoaming agents. Other agents (such as oils and fats) have a more complex behavior and may stabilize some foams at certain concentrations.

The rheology of foam is complex, and viscosity must be measured under flowing conditions. The major things to know are that foams are viscous as well as shear thinning, even when the surfactants and liquid display Newtonian rheology.⁴ This means that foam will suspend solids when the flow stops, and the apparent viscosity decreases as flow increases (when it is being pumped).

Foam Cleaning—Technology

Foam cleaning is a chemical cleaning process that was started in the 1950s. One of the first foam cleaning jobs occurred as a result of a customer’s need for a creative solution to a problem.⁵ An overhead process gas line, 550 ft (167.6 m) of 12-in. (30.5-cm) stock, required cleaning for removal of acetylides prior to dismantling. Acetylides are known to explode when subjected to shock. Although chemical cleaning with an acidic solution was a recognized method to remove acetylides, a “fill and soak” process could not be used because of the piping design. The piping support structure was designed to support only the weight of a gas. A chemical cleaning engineer solved the problem by reducing the density of the acidic solution by converting the liquid to a foam. The job was a success and foam cleaning took a giant step forward. Foam cleaning was soon directed toward the cleaning of utility-type surface condensers.

This method of cleaning seemed like an ideal solution to a cleaning problem. By converting a liquid into foam, the volume is expanded to many times the volume of

the liquid. As a condenser is filled with foam, the vent gases are displaced by the movement of foam through the tubes. Foam enters one water box, flows through the condenser tubes, and exits from the other water box. While the theory seemed plausible, it was soon discovered that many problems existed with this process.

The use of foamed solvents for cleaning surfaces was one of the first technologies patented by the chemical cleaning industry. Early foam generators^{5,6} produced foam by the addition of air or a gas through spargers submerged in the cleaning solution. To obtain a large volume of foam, many spargers were necessary. The spargers could become contaminated with oil from the local air supply, and cause rapid breaking of the foam as it was generated. The spargers also failed from overpressure. If the gas/liquid ratio was too great for the capacity of the generator, generating efficiency was lowered and the result was a poor quality of foam and excess gas. The size of the foam generators made setup sometimes difficult. The first generators weighed more than two tons. See Figure 1 for a more modern design that uses static mixtures.

Despite the problems, the work resulted in the development of useful acid foams and the early model foamers. A foaming agent called G007 was used, but its chemical structure is not now known. These hydrochloric acid foams were not very stable, and the foam generators were large and unreliable. Many of these problems were soon solved by the introduction of a foam generator based on fluid-flow principles⁷ that included a static mixer. However, the new generators failed to solve all the problems. The design of the next generation of foam generators allowed a greater increase of gas flow. The result was a generated foam that had the characteristics of shaving cream; it had good eye appeal but at the sacrifice of efficiency. While many problems were being solved through innovative processes, one predominant problem remained. There was reduced flow through the upper tubes of the condenser during foam cleaning. Many innovative attempts were made to solve this problem but with little success.

To solve the problem, we must look at the foam generation process. Early literature suggested the formation of a cleaning foam by mixing approximately 20 parts of gas with one part of liquid. During the early days, foam samples were collected to determine if the generator was producing this type of foam. It was discovered that if a 1000-mL sample of foam was taken from the foam generator and allowed to break

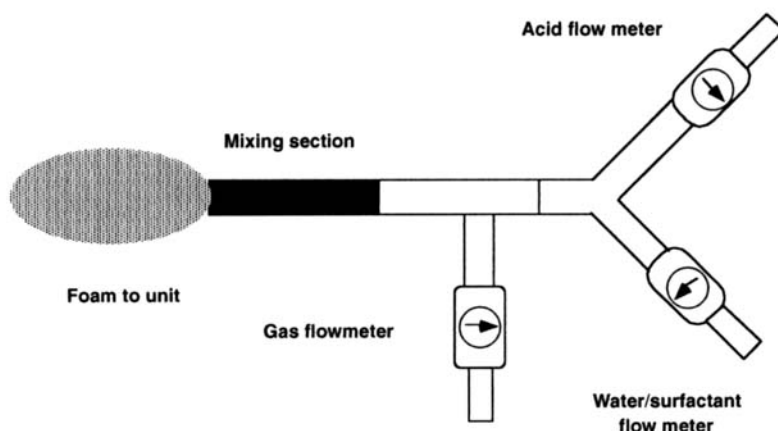


Figure 1. Static mixer (foam generator).

by the addition of a foam breaker, we were producing only a 10/1 ratio of foam to liquid. Where did the excess gas go? The excess gas produced a slug flow pattern of gas and slugs of foam. Slug flow was evidenced on many jobs and was ironically used as a method to determine if foam generation was occurring. Slug flow produced rhythmic pulses in the generator discharge hoses.

Each foam generator is designed to produce a particular type of foam of a given gas/liquid ratio. If we use excess gas to generate foam, the efficiency of foam generation is decreased. For example, in a 100% efficient process, we would use nine parts of gas and one part of liquid to produce 10 parts by volume of foam. If we use 19 parts of gas to one part of liquid to produce 10 parts by volume of foam, our efficiency is 50%—50% foam and 50% excess gas. On actual jobs, a greater excess of gas is used to produce an excellent looking foam. The efficiency is about 20–30%. What happens to this excess gas? The gas is less dense than the foam; therefore it migrates to the top of the condenser box, where it is vented through the upper tubes. If excess gas is always used in the generation of foam, the upper tubes will never have the contact with foam as lower tubes. This was a common complaint from the inception of foam cleaning. Oilfield terminology expresses the ratio of gas to liquid as the foam quality and is defined by the equation $V_g/V_t \times 100 = \text{quality of foam}$, where V_g is the volume of air or gas flow in ft³/min and V_t is the total volume of gas plus the total volume of liquid in ft³/min (1 ft³ = 0.02 m³). This has absolutely nothing to do with foam efficiency, and would be useful only if all liquid and gas components were 100% effective in making foam. This is not the case, as shown by the characteristic slug flow that occurs in most foam generation processes.

Corrosion

There were also unique corrosion problems associated with foam cleaning by using air as the gas phase. When air was used, a cyclical type corrosion process could occur. In the presence of an iron oxide deposit and an acidic foam, the ferric ion would spend on base metal to become reduced to the ferrous ion. Exposure to the oxidant air, present as the gaseous phase of foam, regenerated the ferrous ion to the ferric ion and the corrosion process was repeated. If recycle of the foam cleaning was attempted, the corrosion could become quite severe. The same type of cyclical process could occur in the presence of cupric copper. Cupric copper would reduce on admiralty metal and form the cuprous ion. In the presence of air, the cuprous would be regenerated into the cupric ion for a repetition of the corrosion process. Equations (4)–(7) show the corrosive processes.



The corrosion process could be reduced by the addition of a reducing agent and by using nitrogen, but the cost of a foam job is substantially increased.

Recycle

Early recycle processes completely ignored the gaseous component of foam. The liquid portion was recovered from natural foam breakout or foam breakers and regenerated. The half-life of the foam became an important consideration. Half-life was defined as the amount of time to recover one-half of the amount of liquid used to generate the foam. If a foam did not have sufficient half-life, breakout would occur before the foam completely filled the tube or vessel being cleaned. If the foam had too long of a half-life, natural breakout would not occur and foam breakers had to be used to facilitate breakage. One method included the collection of effluent foam in a large tank to allow more time for breakage. Modern foam formulations are designed to meet almost any foam half-life requirements.⁸

It was soon recognized that a once-through process for foam cleaning was a very wasteful process and it would be desirable to recycle and recirculate the foam through the vessel being cleaned. In a once-through process, the cost of cleaning solutions is directly proportional to the time and flow rate—not on stoichiometric quantities of solvent required to dissolve the scale. A once-through foam cleaning process requires a person on the effluent end to continually spray on a foam breaker. The foam is converted to a liquid, prior to disposal. A new process was developed for the complete recycle of foam cleaning products.⁹ Excess gas is not used because recycle uses only the available volume of gas from the closed system. Recycle foam flow is steady and continuous, and does not depend on excess gas and slug flow for foam generation. The gas phase, liquid phase, and foam are recycled as a closed system or a nonpressure system. Pressure-drop calculations are more realistic. Two-phase slug flow is reduced.

Greater contact of foam in upper condensers can now be achieved because of improved foam flow characteristics. Foamed solutions can now be used until they are completely spent without fear of excessive corrosion problems. It is not necessary to chemically break the foam so it can be recycled as a liquid. Breakout liquid is regenerated into foam using the breakout gas. The process has the advantage of using an inert gas because the gas is also recovered and not wasted in a once-through process. Corrosion additives can be used at a substantial decrease in cost because of recycling. There is less exposure to toxic and irritating gases. Organic cleaning materials can be more economical because of recycle and on-site disposal by incineration. Foaming agents, not completely mixed in the truck, will be mixed in the condenser during recycle with no loss of foaming agents.

Crowe et al.¹⁰ also patented a foam cleaning system that used a fluorocarbon carrier and a stabilizing agent containing a perfluoro alkanesulfonamide. The system incorporated the concept of foam recycle, and the formulation could contain nitric acid to remove hydrocarbon deposits.

New Developments

Kelly reviewed the technology advancements at Corrosion '80.¹¹ These improvements included the more efficient foam generator described above and a surfactant system (based on cationic surfactants) that was less sensitive to metals removed from the deposits than the G007 system. Ball et al. reviewed foam cleaning for boiler subsystems at the 1979 International Water Conference.¹² The highlight of their paper

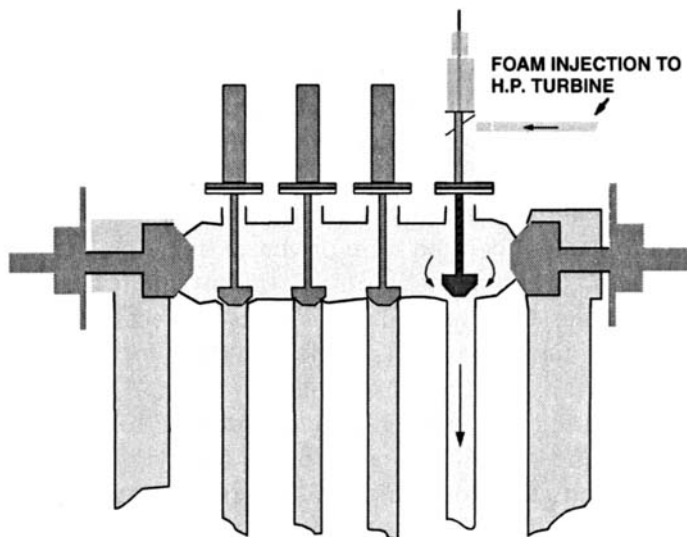


Figure 2. Foamed solvent filling the sections of turbine generators.

was the development of cost/benefit calculations that demonstrated that foam cleaning of utility surface condensers and turbines had an 8/1 benefit/cost ratio.

In 1986, Hoy¹³ presented a paper to the IWC that described a solvent system of foamed HCl, followed by ammonium EDTA and a copper complexer as an improved process for cleaning copper/alloy surface condensers. The complexer reduced the copper “bleeding” that usually follows cleaning of copper metal using hydrochloric acid. Foamed sodium EDTA was used by Flores¹⁴ to remove calcium sulfate deposits from utility surface condensers. Mestetsky and Davis¹⁵ proposed to use a foamed solution of enzymes and nonionic (N-oxides) surfactants to clean batch cokers in refineries. The solution was heated to 210°F (99°C), and the water vapor and foam generated were passed upward into the fractionator, where cleaning took place for 12 h prior to draining of the unit.

Because of the ability of foam to fill large and unusual spaces, it can be used to clean the blades of turbine generators, which become fouled with deposits containing minerals and copper. Very small amounts (25 lb, or 11 kg) can cause the turbine to lose power. With the use of a patented valve,^{16,17} solutions of ammonia and an oxidant (air, hydrogen peroxide) have successfully removed copper deposits from the turbine blades. Figure 2 shows how the foam fills the steam chest and then flows to the turbine sections as the valve is actuated.

PIPELINE SERVICES

Millions of miles of pipelines crisscross the world, transporting products ranging from natural gas to coal slurries. The various types of pipelines may require cleaning for reasons that generally are different from the reasons that process equipment require cleaning. The reasons for cleaning include the following: (1) preoperational cleaning to remove construction debris and to lower the dewpoint prior to introduction of products; (2) operational cleaning to remove debris prior to inspection,

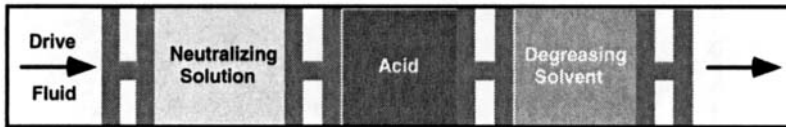


Figure 3. Chemical cleaning pig train.

testing (including hydrostatic testing), and maintenance; and (3) pipeline conversion from one product to a different product (i.e., gasoline to diesel fuel). Any cleaning of pipelines, including conventional use of “pigs,” introduces special problems. First, most pipelines are at “ambient” temperature but are frequently in the temperature range of 40–80°F (4–27°C)—thus, conventional chemical cleaning technologies must function at the lower end of their operational range. Second, pipelines frequently are buried underground or from several feet to thousands of feet (1 ft = 0.30 m) under the ocean—they also run under rivers, cities, or are in isolated geographic areas. Third, usually there are very limited access points, and circulation of “solvents” is frequently impossible.

Mechanical pigs that have scrapers and brushes are used to remove debris from pipelines. For very dirty sections, or for other reasons, “pig trains” of chemical solvents were used to clean sections of pipelines (see Figure 3), using stages of degreasing chemicals followed by acid cleaners and a neutralizing medium. These stages may be many feet long and are separated by mechanical pigs.

In the past 20 years, there have been developments based on the concept of a “gelled pig.” Several patents described the technology. Jaggard and Seales¹⁸ taught the use of a hydrocarbon gelled by an orthophosphate ester. The gel may be used as an interfacial control for different fluids and to remove residual fluids and solids. Scott¹⁹ patented a gelled fluid formed by crosslinking xanthan gum using a multivalent metal (such as ferric sulfate, aluminum sulfate, or chromium chloride). These “Bingham plastic” gels were used to remove debris from pipelines. Purinton²⁰ described the idea of using a gelled fluid as a substitute or as an adjunct to mechanical pigs for cleaning purposes. The underlying concept is that the gelled fluid would be able to flow around obstructions in the pipe (such as probes, changes in diameter) without getting stuck. In addition, the gelled fluid may be able to suspend debris. One of the reasons that mechanical pigs become stuck is that piles of debris build up on the leading edge of the pig as it goes down the pipeline. A pig train that is made up of mechanical pigs as well as segments of gelled fluids is shown in Figure 4.

Several different types of rheological properties may be required for different purposes. Gels that are required to go through geometrically different environments, and to suspend debris, must exhibit pseudoplastic and viscoelastic characteristics and be shear thinning. Fluids containing crosslinked polysaccharides are a type of fluid that exhibits these behaviors. These are known as power-law fluids, in that their rheology is characterized by

$$\mu = k' \gamma^{n'-1}, \quad (8)$$

where μ is the viscosity, γ is the shear rate, k' is the consistency index, and n' is the behavior index of the fluid. Fluids with this type of rheology will become less viscous when sheared (so it will flow around objects) but will suspend debris when the shear rate is reduced.

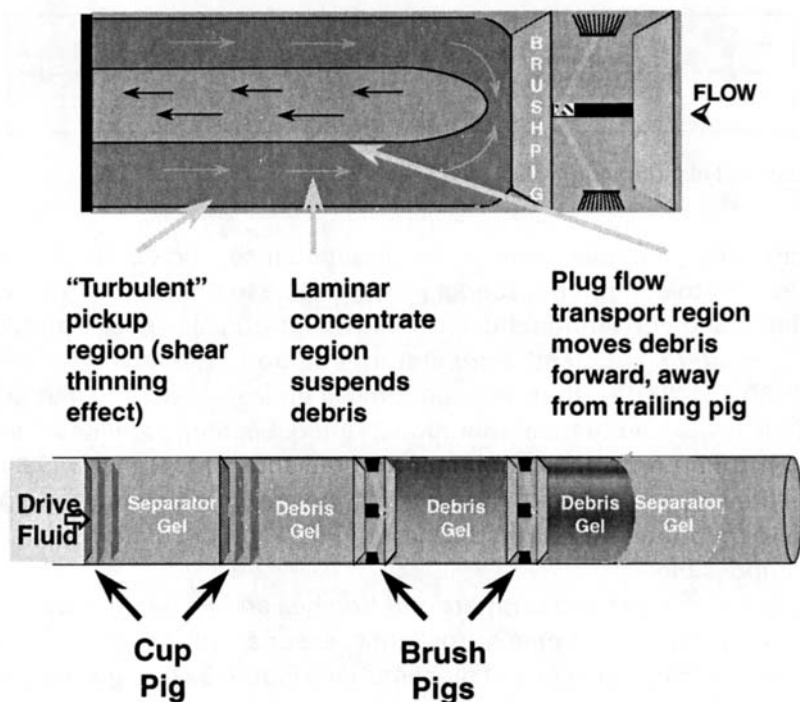


Figure 4. Gelly pig and pig train.

Many specialized gelled pig formulations were developed. The Purinton patent²⁰ noted above used a hydrocarbon solvent that was gelled by using an alkyl oleyl phosphate and an alkali aluminate salt. These gels could be used for dissolving hydrocarbon-like fouling deposits, or for separating various hydrocarbon products. Purinton²¹ also was able to produce a gel of an alcohol (such as methanol) using hydroxypropyl cellulose (HPC). A pig train consisting of water gelled using hydroxypropyl guar (HPG) and crosslinked with sodium borate was followed by the HPC-thickened methanol, followed by a slug of methanol. This sequence was used to remove residual water and thus to dry the pipeline. The HPG gel²² could also be used to remove debris or could be staged with acidic formulations²³ to remove iron sulfide deposits. The HPG gels also can be used to lay down a biocide coating.

One of the largest projects that used gelled pigs was the cleaning of the FLAGS gas line in the North Sea. Scott and Zijlstra²⁴ described this very large job. The FLAGS gas pipeline runs from offshore St. Fergus, Scotland, for 380 miles (611 km) to the Brent gas field in the North Sea. A gelled plug system using a Bingham plastic fluid and plastic scraper pigs was used to remove over 350 tons (317,520 kg) of mill scale and other debris from this line.

A specific use for gelled fluid pigs was described by Keys and Evans.²⁵ A total of 119,000 gal (450,415 L) of gel and degreaser were used to clean about 65 miles (104.5 km) of an abandoned crude oil pipeline that was to be converted to natural gas service. A single, complex pig train was able to clean the line. The train consisted of a number of stages of mechanical and gelled pigs as well as degreaser solutions. Nesbitt²⁶ described the use of gelled pigs to unstick conventional mechanical pigs. The gelled solution was able to bypass several stuck mechanical pigs, remove debris

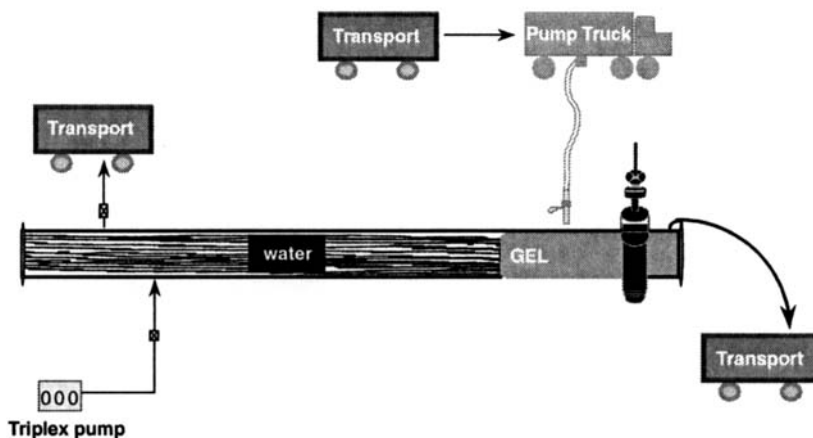


Figure 5. Valve sealing procedure.

from mechanical pigs, and restore the seal. This allowed the drive fluid to push the mechanical pigs to the takeout point.

Gelled pigs can be used for additional purposes (such as part of a paraffin-removal procedure), using hydrocarbon pigs and mechanical pigs and for distributing a corrosion inhibitor film.²⁷

Hydrocarbon gels can be used to help plug leaks in large pipeline valves by delivering a lost circulation material (such as small pieces of cellophane) to the leaking valve.^{28,29} The total isolation of the valves and plugging of all leaks is necessary for a hydrotest of the pipeline to be completed. The method of how a pipeline valve can be isolated by using a gelled hydrocarbon containing cellophane flakes is shown in Figure 5.

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PREFACE

During the past 30 years, there have been significant improvements in the technology utilized to chemically clean industrial equipment. New organic acid and chelant solvents have been developed. New inhibitors and improved techniques for removing refinery/chemical plant deposits have been discovered. Most importantly, there have been significant improvements to our understanding of the chemical mechanisms that underlie many of these processes. This book will review technological areas where there have been new developments that have affected the commercial use of chemicals to clean industrial equipment. The content will emphasize the mechanistic understanding that underlies the important cleaning processes and solvents.

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GENERAL CONCLUSIONS

During the past 30 years many new solvents for inorganic deposits were developed. Low hazard corrosion inhibitors have replaced some of the more toxic materials used to protect the structural surfaces during cleaning. Development of nuclear cleaning methods has extended the life of some very valuable nuclear generating plants. New waste disposal methods have enabled the industry to continue to operate, but have required new chemicals to be developed. Modest improvements for cleaning CP/R equipment include ways to remove FeS and we have seen the development of more environmentally friendly solvents.

These trends will continue and the need for less hazardous chemicals in all areas and disposal concerns will drive much of development. There may be much improved procedures for cleaning CP/R equipment, including improved analytical methods for deposit analyses. There will be more application of computational methods to cleaning technology as computers and software for simulating chemical reactions become more powerful.

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