

## CHAPTER VI

### ACIDIC CLEANING AND OXIDE REMOVAL

Oxide itself falls into the definition of soil. The term pickling for removal of oxides with acidic materials is probably derived from the early use of vinegar (acetic acid) for this purpose. By analogy, removal of oxides with alkali is sometimes loosely referred to as alkaline pickling.

Acid is used for removal of

1. Mill scale (hot-rolled scale) developed during hot forming of metal.
2. Scale developed during welding.
3. Scale developed during heat treating.
4. Superficial oxide which interferes with painting, porcelain enameling, tinning, galvanizing, or electroplating, etc.\*
5. Rust and corrosion products.
6. Proteinous deposits.
7. Hard water scale.
8. Products of reaction of hard water with soil, especially protein (milkstone, beerstone).

The acids used for these purposes have been described in Chapter 2.

#### **Pickling Plain (Low Alloy) Steel**

Steel may be covered with mill scale due to original hot rolling or to hot forming of steel.

Mill scale or "fire scale" consists of three layers of iron oxides; ferrous oxide, magnetic iron oxide ( $\text{Fe}_3\text{O}_4$ ), and ferric oxide, the last outside layer being the thinnest. Magnetic iron oxide is attacked least by sulfuric acid and, reportedly, is removed only after reduction by the hydrogen released during reaction of steel and acid. Moreover, the ferric oxide of mill scale differs from that in rust; the latter is more easily removed by acid when not excessively dehydrated.

If hot-scaled steel is cooled rapidly the ferrous oxide layer is thick and impervious; if cooled slowly some of this layer decomposes to magnetite and iron, with coincident cracking. Acid penetrates the cracks and attacks the ferrous oxide. Pickling is much more rapid because of the galvanic cells set up between the iron and magnetite; usually the determining rate in pickling becomes that of penetration of the cracks.

Acid converts iron oxide to a soluble salt while reaction with iron yields

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\*The light etch obtained at the same time is beneficial for adhesion due to extension of the surface area.

INDUSTRIAL CLEANING

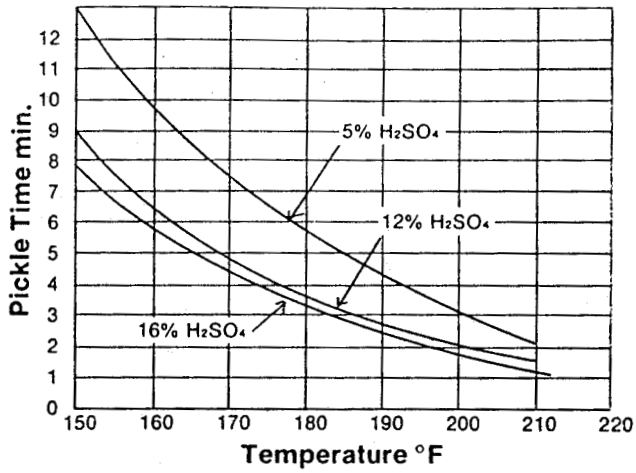


Fig. 6-1a Time temperature relationship for pickling hot-rolled plain carbon steel in 5, 12, and 16% sulfuric acid solutions (by weight).

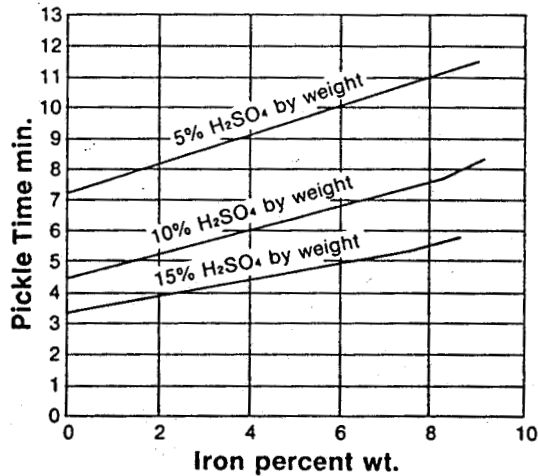


Fig. 6-1b Effect of dissolved iron on the time of pickling at 140°F.

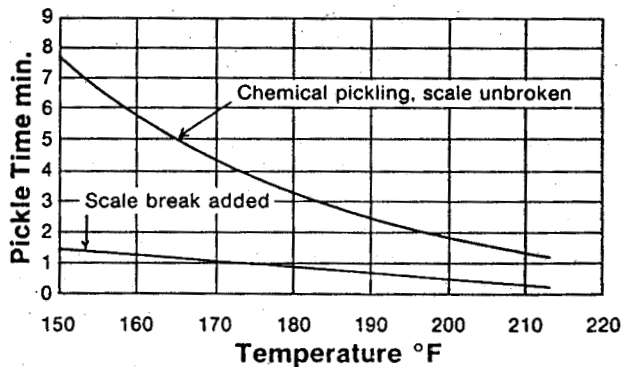


Fig. 6-1c The effect of scale breaking on pickling time for hot-rolled plain carbon steel (16% sulfuric acid by weight). (Courtesy National Electric Products Corp.).

hydrogen gas and an iron salt. The generation of hydrogen is very important, not only as it may relate to reduction of magnetic iron oxide (as indicated above) but because it undercuts the scale and causes it to flake off; some authors consider scale to be sufficiently porous so that acid penetrates through to the metal.

When steel is in continuous form, as in sheet, wire, rod, or tubing, mechanical deformation may be used in conjunction with pickling to accelerate scale removal. This loosens the scale and permits faster penetration with acid.

Much mill scale is removed discontinuously at the fabricating plant as well. Here some loosening of the scale may occur during manufacture but a more frequent assist is partial rusting of hot-rolled stock during storage. This rusting tends to be greater in areas where the mill scale has been loosened by mechanical shock. Usually rusting makes subsequent pickling easier but a longer treatment may be necessary to remove the rust at the bottom of the pits causing greater metal loss and a rougher surface.

Heavy mill scale or oxide developed by exposure of steel to heat, as in rolling, welding or heat treating, is removed industrially with hot sulfuric acid. Being a straightforward chemical reaction, the rate of pickling is increased with increase in concentration and temperature. Thus, the pickling rate goes up proportionately as concentration is increased from 0 to 25% (volume) of sulfuric acid; above 25% the pickling rate goes up more slowly. The effect of temperature (Fig. 6-1a) is a doubling of pickling rate for each rise of 15 to 20°F between 70 and 210°F. Agitation is of considerable assistance. Spray pickling is far more rapid and uniform than immersion pickling (partially because it avoids trapped gas pockets that prevent contact with the acid when parts are "nested") while pickling with a jet of acid or with agitation through ultrasonics is very rapid. Air agitation helps by permitting fresh acid to come in contact with the surface.

As the concentration of iron in the pickle bath increases, the pickling rate is reduced (Fig. 6-1b). At a concentration of iron of approximately 5% the rate is halved for a 10% sulfuric acid bath. A 5% iron-containing bath has 25% iron sulfate hydrate.

In industrial pickling these factors are balanced for greatest economy of time, heat, and chemicals. The most common conditions are as follows: sulfuric acid, 5 to 15% by volume, temperatures 140 to 180°F, time, 5 to 45 min. If the most usual condition were stated it might be 10% by volume, 160°F, for 15 min.

For economic reasons, as well as disposal problems, the acid bath is often charged at, say, 10% by volume and replenished to maintain close to this strength. As the iron buildup approaches 5% the concentration is allowed to drop to about 5% of acid, allowing longer time for pickling; then the bath is discarded. In waste disposal it is usually necessary to neutralize all or part of the residual acid.

The sulfuric acid pickling bath is also used to remove rust from steel or other corrosion products from other metals. Most rusts on plain carbon

steel are far easier to remove than mill scale. Some require more time because of the necessity for removal of rust from deep pits. In general, rusts that develop in a humid but otherwise normal atmosphere are fairly easy to remove. Rusts that develop on oily steel (see later) or in some corrosive atmospheres, or rusts that are very old and dehydrated, are quite difficult to remove. Sometimes hydrochloric acid is effective in these cases when sulfuric acid is not.

Hydrochloric acid is most frequently used at room temperature by dilution of commercial concentrated acid with 1 to 3 parts of water. It is convenient for use at room temperature if the higher cost of the acid, the fumes, and some tendency toward pitting can be tolerated. Dilution with an equal volume of water is the most common pickling bath. Hydrochloric acid tends to leave less pickle smut than sulfuric acid. Even in some mill operations, therefore, it is not uncommon to have a short final treatment in this acid (e.g., 10 to 25% volume for 2 to 5 min.) after sulfuric acid pickling. The addition of common salt (rock salt) to the extent of 2 to 10% of sulfuric acid generates some hydrochloric acid without excessive fumes which can yield some benefits with minimum disadvantage.

There has been a trend in recent years towards the use of hydrochloric acid in larger scale pickling of sheet steel, etc. (3) at the mill. A prime reason is that the acid can be largely exhausted prior to being discarded, thereby reducing the waste disposal problem.

Thus, the acid can be used down to concentrations of 2% while the iron content can be allowed to rise to 8% in contrast with sulfuric acid which is ineffective and is usually discarded when the iron content rises to 5% while still containing 5% acid.

Because of the tendency towards pitting and rapid action on the base metal hydrochloric acid is usually used with a pickling inhibitor, often as a formulated proprietary composition. Pickling accelerators are discussed later.

Phosphoric acid is used to remove rust and corrosion products when pitting and rerusting must be minimized. Smut is produced to a lesser extent than with sulfuric acid but more than with hydrochloric but reduced acid attack on the metal also tends to reduce the amount of smut. The lower pickling rate plus the greater cost of phosphoric acid limits its use in large operations. Special phosphoric acid systems were discussed in Chapter 2 (9).

Phosphoric acid is not as corrosive in concentrated form as sulfuric acid or nitric acid, does not fume like hydrochloric, nitric or hydrofluoric acids and will not attack stainless steel as does hydrochloric or sulfuric acids. Because of this it is widely used to remove hard water scale, proteinous deposits, milkstone, beerstone, etc. from stainless steel in the food processing industries. For these purposes it is combined with compatible surfactants to provide removal of organic as well as inorganic soils. These may be of high or low foaming types as equipment and agitation requirements dictate. Nitric and hydrofluoric acid is used for brightening aluminum and stainless steel.

### Pickling Oily Steel

This represents a special industrial problem that deserves attention. Such surfaces are found with steel treated with a rust-preventive and then weathered or aged so severely that the oil-base rust inhibitor fails to prevent rust formation.

For less severe rusting cases the formulated phosphoric acid cleaners may be used. This is an important application for these materials, especially as a "spotting" operation for patches of rust where a formal pickling step is not available and parts are not too severely weathered. These products contain surfactants and solvents which penetrate the residual oil.

When oily work is introduced into a hot acid bath the oil may be reasonably well removed by melting and gathering of the oil at the operating temperature and undercutting of the oily globules by gas generation. Soaps are decomposed to fatty acids, molten at bath temperature. However, the bath is unable to emulsify the oil that floats and tends to cling to the work as it leaves the bath. Much soil is not removed and prevents further action of the acid. If the oil were first removed by an alkaline cleaner and then placed in acid, a fresh layer of soil may be exposed after removal of superficial rust by the acid.

One approach is awkward, namely, alkaline clean, rinse, pickle, rinse, alkaline clean, rinse, pickle, rinse. A widely practiced procedure which frequently assists cleaning is to add an acid-stable wetting agent to the pickle bath to aid in oil removal. Phosphoric acid baths rich in surfactants and organic solvents (water soluble) sometimes take care of this problem but a better solution is to use alkaline rust remover (Chapter 7).

### Activation Pickling

For applications such as enameling, tinning, galvanizing, or electroplating there is the necessity to remove light oxide. Oxide would reduce adhesion of the surface coating while light etching of the surface assists adhesion or penetration since a larger surface area is available to adhere to.

Sometimes other chemicals are added to influence etching of the surface. This type of treatment is not limited to steel; it is important for stainless steel or nickel which are passive due to the presence of extremely coherent oxide films on the surface. By removal of these the surface is said to be activated.

Acid dips prior to plating may consist of  $\frac{1}{2}$  to 10% sulfuric acid, 1 to 25% hydrochloric acid or 2 to 25% phosphoric acid, but also would include 2 to 10% acetic acid, 1 to 10% citric acid or the other organic acids that are good sequestrants for metal ions. In general, the acid treatment is as short as possible to avoid the possibility of gas absorption; this gas would later be released under the electroplate and cause blisters (see hydrogen embrittlement). Fluoboric acid dips are often used when the plating bath is a fluoborate bath.

Organic acids are used in acid treatment prior to electroplating. These include two strong acids, oxalic acid and trichloroacetic acid, but

slow-acting acids, such as citric, acetic and hydroxyacetic acids, are also used. These sequestering acids are also used in conjunction with acid for brightening (4). Chemical polishing of metals in acidic baths is sometimes treated as a pickling operation but will not be considered here. Information on this may be found in books such as Wernick and Pinner, "Finishing of Aluminum;" Graham, "Electroplating Engineering Handbook", section by Faust; and W. J. McTegart, "Chemical Polishing of Metals," 2nd Ed., Pergamon Press.

### **Pickling Stainless Steel and High Chrome-Nickel Alloys**

The stainless and corrosion-resistant characteristics of high chromium-nickel alloys of iron are due to the presence of a tightly adherent, non-porous oxide layer. Since there are a considerable number of alloy steels, not all of which are "stainless", the composition of the oxide would vary accordingly. Studies indicate that the oxide layer (5) on stainless steel is composed of certain forms of chromic oxide, alone and in solid solution with iron and manganese chromites and nickel oxide.

Sometimes the heavier scales from an oxidizing atmosphere in the furnace are easier to remove than those formed when steel is annealed in a reducing atmosphere, high in hydrogen. When the latter develops some oxygen content, thin oxide films are formed which are quite difficult to remove by acid pickling. Sometimes further oxidation will provide easier pickling. If austenitic stainless steel is annealed in an atmosphere-controlled furnace with soils that can be carbonized, metal carbides may form. Selective pickling can occur at these areas resulting in pitting and excessive attack. Segregation of carbides may develop during welding if stabilized stainless steel, e.g., types 316, 317, or 347, is not used. Moreover, highly stressed alloy steels are susceptible to hydrogen embrittlement and indiscriminate pickling may lead to cracking of the parts during subsequent service.

The difficulty of removal of scales from stainless steels and some high chromium alloys has focused attention on this subject and a variety of baths have been proposed. One such system uses sulfuric acid (10% volume), rock salt (4 oz/gal), temperature 160 to 180°F, followed by hydrochloric acid (25%), nitric acid (3%) temperature 140 to 160°F as a double cycle for conditioning and removing heavy scale.

Austenitic stainless steels may also be pickled in a ferric sulfate-hydrofluoric acid mixture. This pickle is also used on straight chromium steels but these should first be treated in sulfuric acid (8 to 19% vol., 150 to 170°F). This system does not require an inhibitor. Spencer (6) has provided some data comparing this pickle with sulfuric acid. The ferric sulfate-hydrofluoric acid may result in excessive loss of metal and must be carefully controlled. Conditions that have been recommended for this bath are as follows: Ferric sulfate 6 to 8%, hydrofluoric acid (100%) 1.8 to 2.0% temperature 160 to 180°F, or ferric sulfate 10%, hydrofluoric acid 1 to 2% temperature 120 to 140°F. In another method 5 to 10% ferric sulfate is added to 8 to 12% (vol.) sulfuric acid at 150 to 170°F.

All of the baths reviewed above are followed by a nitric acid pickle. This is 10 to 20% by vol. of commercial nitric acid in water plus 1 to 4% hydrofluoric acid and is used at 120 to 150°F. As mentioned earlier, these acids must be handled with great care and fume exhaust systems must be provided. A common bath would be 15% nitric, 2% hydrofluoric at 130°F for 10 to 20 minutes. This is followed by thorough rinsing. Even though fluoride causes less pitting than chloride, the danger of some pitting is still present. In a sense the nitric and hydrofluoric acids work against one another in this respect; the higher the nitric acid content the less the danger of pitting and excessive metal lost, if pickling times and temperatures are reasonable.

Care must be taken to avoid excessive contact with acids containing chlorides to minimize pitting, to which stainless steel is quite susceptible. Otherwise the factors involved in pickling are as previously discussed for plain steel, except for much slower action. Pickling inhibitors or accelerators and foam blanket agents may also be used as for plain steel. After removal of the oxide by pickling, the metal may require passivation, re-establishment of the oxide film, usually by use of greater than 20% by volume of nitric acid.

The removal of some scales from stainless steel is so difficult that these baths will sometimes be found inadequate. This is especially true of alloys such as Hastelloy, certain high nickel or cobalt alloys, and scale induced by exposure to high temperature conditions. This, coupled with the sensitivity to hydrogen embrittlement of many high strength alloys, has resulted in the development of alkaline descaling baths, including those used in molten form at high temperatures (Chapter 7). Sometimes these condition the scale for removal by acid.

### **Acceleration of Pickling**

Rate of pickling varies with the alloying elements and carbon content. Carbides in steel provide areas for electrogalvanic action which facilitates pickling. Variations exist, occasionally of considerable magnitude, in the rate of attack on cold rolled SAE 1010 steel. An informal report\* indicates a variation within a group of approximately 20 heats of steel in which the highest rate was double the lowest. Much of this is related to rolling practice. Addition of salt or muriatic acid to sulfuric acid accelerates the pickling rate of both plain and stainless steel. There are other materials which are potent accelerators although not to the same extent for all steels. One such material is sodium or potassium ferrocyanide used at 1 to 2%. This is more effective on plain steels.

For stainless and medium-alloy steels, the addition of  $\frac{1}{2}$  to 2% of sodium thiosulfate, sodium hydrosulfite, or sodium sulfite can increase pickling rate markedly.

Another way of accelerating pickling action is by electrolytic pickling

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\*Private communication, Dr Ludwig Schuster.

(later) or by ultrasonic pickling (Chapter 5). Cathodic pickling is much faster than nonelectrolytic or anodic pickling.

### **Pickling Inhibition**

It is desirable to have minimal attack on the base metal. This is only partially correct since reaction between the acid and metal to form hydrogen gas is a factor in pickling, as has been discussed. However, excessive reaction with the metal consumes acid, creates fumes, enhances hydrogen embrittlement, produces smut, and may remove enough metal to affect tolerances.

A number of materials are effective in reducing the attack on the metal with minor (but significant) reduction in the rate of oxide removal. These may be classified as:

1. Nitrogen and sulfur-bearing materials occurring naturally in such products as glue, beer fermentation dregs, flour, etc.
2. Nitrogenous coal tar-derived chemicals; such as still residues, or more refined chemicals like quinaldine, substituted pyridines, etc.
3. Synthetic sulfur and/or nitrogen-bearing chemicals like dibutyl thiourea, ditolyl thiourea, hexamethylenetetramine, etc.
4. Certain salts which plate out the metal by galvanic action, e.g., arsenic, molybdenum.

The first group is more of interest from an historical viewpoint although they are still used. They are less effective and more troublesome than the others.

Inhibitors in acid solution are normally evaluated on oxide-free metal specimens. Thus, clean steel is so protected from acid attack by the presence of good inhibitors that the rate of metal removal with sulfuric, hydrochloric, or phosphoric acids is reduced by 95 to 99%.

It is established that the inhibitor is adsorbed on the surface since inhibiting effects persist after withdrawal of the metal from the acid bath and insertion in another uninhibited bath. The residue that remains sometimes has to be removed; some require a hot alkaline cleaner treatment to effect complete removal. A large number of proprietary formulations have been developed in an effort to obtain maximum inhibition of attack on metal with the fewest undesirable residues. Many contain foam blanket-generating materials to keep fuming to a minimum and to provide some cleaning and wetting-out action. Care should be taken to avoid local overheating of inhibited acids since this may destroy the organic inhibitor.

### **Hydrogen Embrittlement**

The absorption of hydrogen gas developed during pickling or cathodic electrocleaning causes embrittlement of stressed steel. This shows up as a sharp increase in the tendency to fracture after bending, early fatigue failure on repeated flexing of a specimen, or in a lower force required to break notched specimens, as well as in performance failures under conditions of repeated stress.

High carbon and medium chrome steels are especially sensitive to hydro-



gen embrittlement after deformation. The extended use of these alloys in aircraft and missile applications and the failure of parts, only slightly embrittled, after prolonged use, has focused attention on this problem (7).

If parts with absorbed hydrogen are heated, part or all of the gas is emitted. Thus, heating a piece of pickled tool steel in oil at 300°F gives a considerable stream of gas. While there are no fixed rules, most of the hydrogen is released by heating for 1 hour at 300°F, 2 hours at 210°F, or even by room temperature storage for a month. For some of the critical chrome alloys used under high stress, oxides must be removed in an alkaline system (Chapter 7).

### Pickling Smut

When steel is pickled a smut is left behind, the amount of which is governed largely by the carbon content of the steel, the length of pickling time, and the type of acid used. Cast iron, which has a high carbon content, is especially prone to smut formation. Overpickling increases smut formation.

It is probable that the most significant component of the smut is ferric carbide, insoluble in sulfuric acid but soluble in hydrochloric acid. In fact, complete solution of a high carbon steel specimen in sulfuric acid leaves a powder which analyzes close to the ferric carbide content of the steel. Most smut also contains some iron oxide and finely divided carbon.

Pickling smut may be removed by ultrasonic cleaning or by electrocleaning at high current densities in alkaline electrocleaner (Chapter 5) or by anodic electropickling, sometimes called the "Madsenell Process" (3). This process uses higher than 85% sulfuric acid at room temperatures to 100°F. Current density is 50 A/sq. ft. but current passage ceases after  $\frac{1}{2}$  to 10 min. This removes adsorbed gases as well as smut. It can passivate the surface so that re-rusting is prevented. For this purpose a bath may be used containing 30% (v/v) sulfuric acid and 3 oz/gal of potassium dichromate, at about 100 A/sq. ft.

The Bullard-Dunn process is used, not only to prevent rerusting, but also to prevent overpickling. It is a cathodic electrolytic process carried out in a solution composed of sulfuric and hydrochloric acids plus a tin or lead salt.

4.75 g/liter conc. sulfuric acid

10.3 g/liter commercial hydrochloric acid

22.5 g/liter sodium chloride (lead and duriron anodes, the lead dissolving or lead salts added to 1 g/liter)

60 to 75 A/sq. ft. at 150 to 180°F

or

100% sulfuric acid

1g/liter of tin salt

60 to 75 A/sq. ft.

140 to 150°F

Duriron anodes

The lead or tin desposits as soon as the oxide is removed and the steel exposed. The tin or lead prevents further attack by the acid and protects the steel from re-rusting. When necessary the tin or lead is stripped by treatment with strong alkali.

### **Prevention of Rerusting**

A moist, clean steel surface with mildly acidic residue rerusts very rapidly.

Rerusting can be minimized by rapid dry-off and by maintaining the part submerged in cool water prior to a rapid dry-off. If the water is alkaline it is far better; soda ash or lime is often used in the final rinse to prevent rusting during handling. Sodium nitrite solutions of from 0.1 to 10% concentration, depending on the time of storage, is often used as a final rinse (and can be quite effective) for those cases where the parts should not be covered with an oily rust preventive. Otherwise a water displacing rust preventive may be used.

### **Nonferrous Metals—Aluminium**

Phosphoric acid type cleaners do not etch aluminum under mild operating conditions and so some cleaning is performed with this type of cleaner, although alkaline cleaners are normally superior detergents.

Hydrochloric acid removes oxide from aluminum with considerable etching, though not with as esthetic an appearance as in alkaline etching. Addition of stannous chloride to hydrochloric acid gives a deeper etch. Hydrochloric acid is not normally used for cleaning aluminum.

However, phosphoric acid plus hydrofluoric acid is used for cleaning and brightening aluminum. Surfactant may be added so that cleaning and brightening are obtained simultaneously and this type of system is used industrially. It is followed by a good rinse. Field application of this type of product for cleaning trucks, aircraft, etc. is more usual. Care must be exercised with regard to total concentration of fluoride and temperature to avoid excessive loss of metal.

The organic acids, citric, gluconic, hydroxyacetic, etc. find application in aluminum cleaning, frequently in combination with phosphoric acid, as in removal of buffing compound, etc., without etching bright or smooth aluminum.

One important area in acid aluminum cleaning is in the removal of oxide prior to spot welding. In this application reestablishment of the oxide film must be uniform and preferably slow. Acid cleaners containing chromate are used widely. The chromate bath develops a uniform, "tight" oxide deposit which grows in thickness slowly and uniformly. This property is measured by electrical resistance change. A popular instrument for this is the G. E. microhmeter.

Acidity or chromate content are variously more important dependent on operating conditions. Experience has shown that lower concentrations of one or the other are sometimes better. In some instances the deoxidizer is more effective at lower acidity and sometimes the reverse is true. Unfortunately,