Troubleshooting

# Stainless Steel Surfaces in LC Systems, Part I — Corrosion and Erosion

Guest Authors
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**Stainless steel is inert — or is it?**

***Editor's note:*** *Many workers consider the stainless steel components of their liquid chromatography (LC) systems to be inert to attack by any chemical to which they might be exposed. In this first part of a two-part series, the authors share their considerable expertise on the chemical interactions of stainless steel. In this month's "LC Troubleshooting," they discuss the general characteristics of stainless steel. Next month, they will focus more closely on the use of stainless steel in LC systems and some recommendations for avoiding problems.*

**John W. Dolan**
LC Troubleshooting Editor

Liquid chromatography (LC) users seem to fall into two groups: those who assume the inner surfaces of their chromatographic systems are inert and therefore never interfere with the chromatographic process and those — mainly biochromatographers, ion chromatographers, and electrochemists — who know that the surfaces within their systems present real and persistent threats to their work. We were blissful members of the former group until the day we decided to clean the cell of a UV–vis detector with dilute nitric acid. The manual from the manufacturer recommended using 50% nitric acid, prepared by mixing equal volumes of concentrated nitric acid and water, with a 10-min contact time. However, being chemists, we decided to use a more dilute and less hazardous 20% nitric acid solution for a correspondingly longer contact time of 30 min. After this soaking period, the nitric acid had a rusty tan color which we interpreted to be accumulated crud being removed. However, after two more, even longer, contact periods with fresh 20% nitric acid, the tan color continued to be washed out. We were dissolving our detector cell.

Several simple laboratory tests showed us that nitric acid at concentrations of 10–30%, which corresponds to 1.5–5 mol/L, corroded small samples of stainless steel but that more concentrated nitric acid — 50–100% or 7.5–15 mol/L — did not. We thought we had discovered something new — until we found that this strange concentration dependence has been known for centuries (1) and was studied extensively by Michael Faraday in the 1830s (2). Thus, chromatographers who use nitric acid for cleaning or passivating the inner surfaces of their LC systems should have at least some awareness of the vulnerability of their stainless steel surfaces to corrosion processes in general and to nitric acid in particular.

In this installment of "LC Troubleshooting," we will treat the general topic of stainless steel corrosion briefly, with an emphasis on processes whereby a protective passivation layer is formed or destroyed by chemical reactions with the environment. We also will discuss reactions involving nitric acid, including the Faraday paradox phenomenon, and recommendations relative to the maintenance, plumbing, and replumbing of LC systems. We will discuss several aspects of stainless steel corrosion and passivation in relation to LC components that contact aggressive mobile phases. We will describe the concentration dependence of aqueous nitric acid as a cleaning and passivating agent for stainless steel surfaces and the recommendation that carefully prepared 50% (7.5 mol/L) nitric acid be used only as a last resort for cleaning and passivating LC system surfaces. Users can substitute Hastelloy C22, titanium, or PEEK tubing and frits for those made of stainless steel to minimize corrosion problems.

## Stainless Steel

Stainless steel has long been a material of choice for fabricating analytical instrumentation system components because of its machinability, ductility, hardness, strength, inertness, and low cost. Most LC systems have stainless steel surfaces that come into direct contact with the mobile phase involved in the chromatographic process. These inner stainless steel surfaces, as most surfaces, tend to acquire a thin layer or local deposits of adsorbed materials. The corrosion of stainless steel surfaces, although not initially a serious problem, can develop gradually and eventually become difficult and expensive to resolve.

Stainless steel is a large family of iron-based alloys, a dozen or more of which have been used in LC systems. Type 316 is the most widely used stainless steel in LC systems and other analytical instruments because of its favorable balance of properties such as hardness, machinability, and corrosion resistance. Thus, we will use type 316 stainless steel as our reference material. Other types of stainless steel often are selected for some especially useful property, such as type 303 for machinability, type 304 for ductility, type 316L for weldability, and type 321 for its resistance to stress corrosion. Stainless steel tubing and other metals that have special properties can be used in different components of an LC system — for example, pumps, injectors, other valves, and detectors — without causing serious corrosion problems for most applications (3). However, corrosion of all types of stainless steel surfaces occurs continuously in most nonvacuum environments. We — and civilization in general (4) — are fortunate that corrosion is very slow in many applications.

## Corrosion and Passivation

Pickering (5) listed several conditions that support stainless steel corrosion processes in LC systems. One condition is low pH; others are the presence of reducing agents (hydrochloric acid, dimethyl sulfoxide, and phenol), chelating agents (citrate, chloride, EDTA), strong ligands (dimethyl sulfoxide, phenol, certain anions), and some salts, especially those containing chloride or lithium ions. Shoup and Bogdan (6) discussed factors that affect stainless steel corrosion from electrochemists' viewpoints. Their discussion is based on the use of electrochemical detection, which is highly sensitive to the presence of even traces of iron corrosion product species that are produced along the mobile-phase flow path. Mowery (7) showed that fast flow rates in flow-control valves and the abrupt changes in flow direction inherent in injection valves sometimes can cause very rapid local corrosion by LC mobile-phase solvents.

In general, chromatographers should be aware of Bristow's observation (8) that mixtures of mobile-phase components that individually are inert to stainless steel can become corrosive in combination. Examples of this phenomenon are " . . . halide impurities un-ionized and inactive in halocarbons, but ionized and active in mixture with hydroxy solvents (such as methanol) and acids inactive in aqueous solution, but very corrosive in aqueous acetonitrile solutions."

Stainless steels such as types 316, 303, 304, and 321 are iron-based alloys with various noniron elements, mainly chromium and nickel, in proportions of roughly 70% iron–18% chromium–8% nickel (9). Both the surface and the bulk distribution structures of the atoms in a given piece of stainless steel typically are very complicated because they depend on the thermal history and the extrusion and machining process history of each piece (10). Furthermore, the properties, including the corrosion behavior, are determined largely by these structures. As a further complication, the range of compositions that can be classified as a given type of stainless steel is sufficiently broad, so even if you consider only one type of stainless steel, the corrosion behavior of pieces cut from different sources can vary greatly under the same environmental conditions.

Separately or collectively, the metal atoms in stainless steel are unstable in air, air-containing solutions, and in many other environments with respect to the formation of oxides or other products. Controlled oxidation of a stainless steel surface by oxygen or another suitable oxidizing agent such as nitric acid produces a thin oxide layer, called the *passivation layer.* This layer is typically only several nanometers in thickness, and it functions as the surface's line of defense against rapid attack by modestly aggressive environments (11).

The passivation layer is quite complicated structurally, nearly as complicated as the stainless steel itself (4,10). Thus, we won't attempt a detailed description in this column, but we will discuss several fundamental aspects of the formation and destruction (that is, dissolution) of the passivation layer in a simplified but informative way.

Consider the bare metallic surface of a piece of stainless steel as if it were pure iron. In the presence of an electron-accepting or oxidizing reagent, the contact of the iron surface with an aqueous phase permits the production of $Fe^{2+}$ (equation 1). Molecular oxygen, for example, can accept electrons in acidic (equation 2), neutral, or basic (equation 3) media. Many other oxidizing species can accept the electrons just as well.

$$Fe^{\circ} \rightarrow Fe^{2+} + 2e^{-} \qquad [1]$$

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \qquad [2]$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad [3]$$

A Pourbaix diagram can provide an impression about how metal oxide corrosion products relate to the oxidizing power (that is, the electrical potential [*E*]) and to the pH of an aqueous solution in contact with the metal surface (12). Figure 1a is a simplified Pourbaix diagram for an iron–aqueous solution oxide system. Each region of the figure represents an equilibrium situation for the corresponding *E* value and pH of the aqueous solution. It is

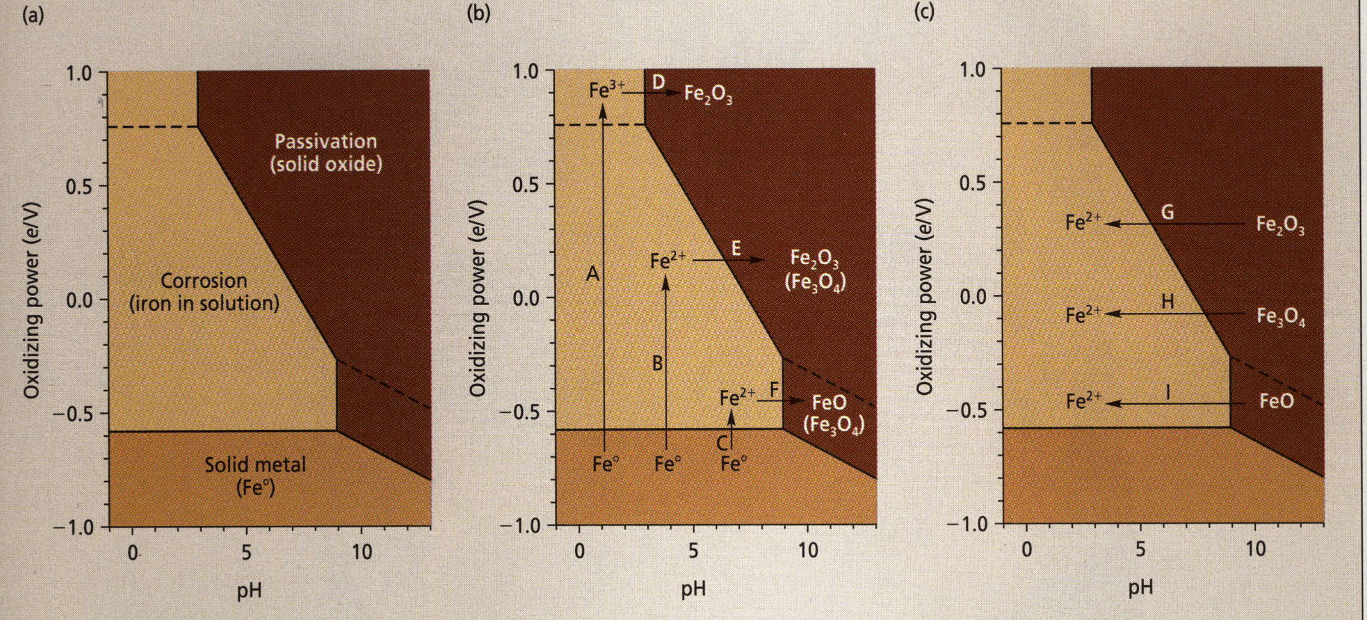

**Figure 1:** Pourbaix diagrams showing (a) equilibrium relationships between iron, iron oxide and solution phases, (b) the reaction path toward metastable oxide layer formation (passivation), and (c) passivation layer destruction by acid media.

not very useful, however, to think only about the equilibrium situation, because the equilibrium merely indicates that all of the metal tends to remain as metal under reducing conditions, and all of the metal eventually dissolves or forms an oxide (rust) under oxidizing conditions. It is more useful to think about the early steps that can occur on the way toward equilibrium. Figure 1b indicates a two-step route to oxide-layer formation. The metal surface first is oxidized to produce $Fe^{2+}$ or $Fe^{3+}$, then rapid reactions produce a thin, metastable, oxide layer on the surface. This result normally is not an equilibrium, because dissolution reactions also occur under neutral to acid conditions (Figure 1c). The overall picture becomes one in which both oxide layer formation and dissolution can occur in a continuing way.

Figure 2 shows a cross-section of an oxide layer to illustrate how formation and destruction processes can occur simultaneously. The resulting migration of the oxide layer, with corresponding loss of the underlying metal, occurs by formation of new oxide *through* the existing oxide layer. Typically this process is long and slow. A plausible mechanism for the migration of the oxide layer is based on the point defect model (4,13). The point defect model involves diffusion of vacancy-defect species through the oxide layer (Figure 3), which allows the production by oxidation of metal ion species at the metal-oxide interface. Note that the diffusion of vacancies is a step-by-step process, not a concerted process. Figure 3 is an idealized representation designed to suggest the physical aspects of vacancy-defect diffusion as it relates to corrosion-migration of the oxide layer. McDonald (4,13) described the chemical aspects of the overall process.

The point defect model also provides a plausible description of the development of local pit corrosion, a form of corrosion that is particularly bad in instrument systems. If for whatever reason the oxidation step is blocked locally and only oxide vacancies arrive at the metal-oxide interface, these oxide vacancies presumably can coalesce to form a thin, open gap, as pictured in Figure 4a (4). The gap blocks the migration of the oxide layer in that region (Figure 4b) and permits the ongoing dissolution process to eventually open a direct attack on the underlying metallic layer by the solution phase.

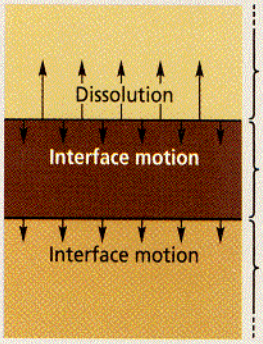

**Figure 2:** Cross section of an oxide layer on a stainless steel surface under steady-state formation–destruction conditions.

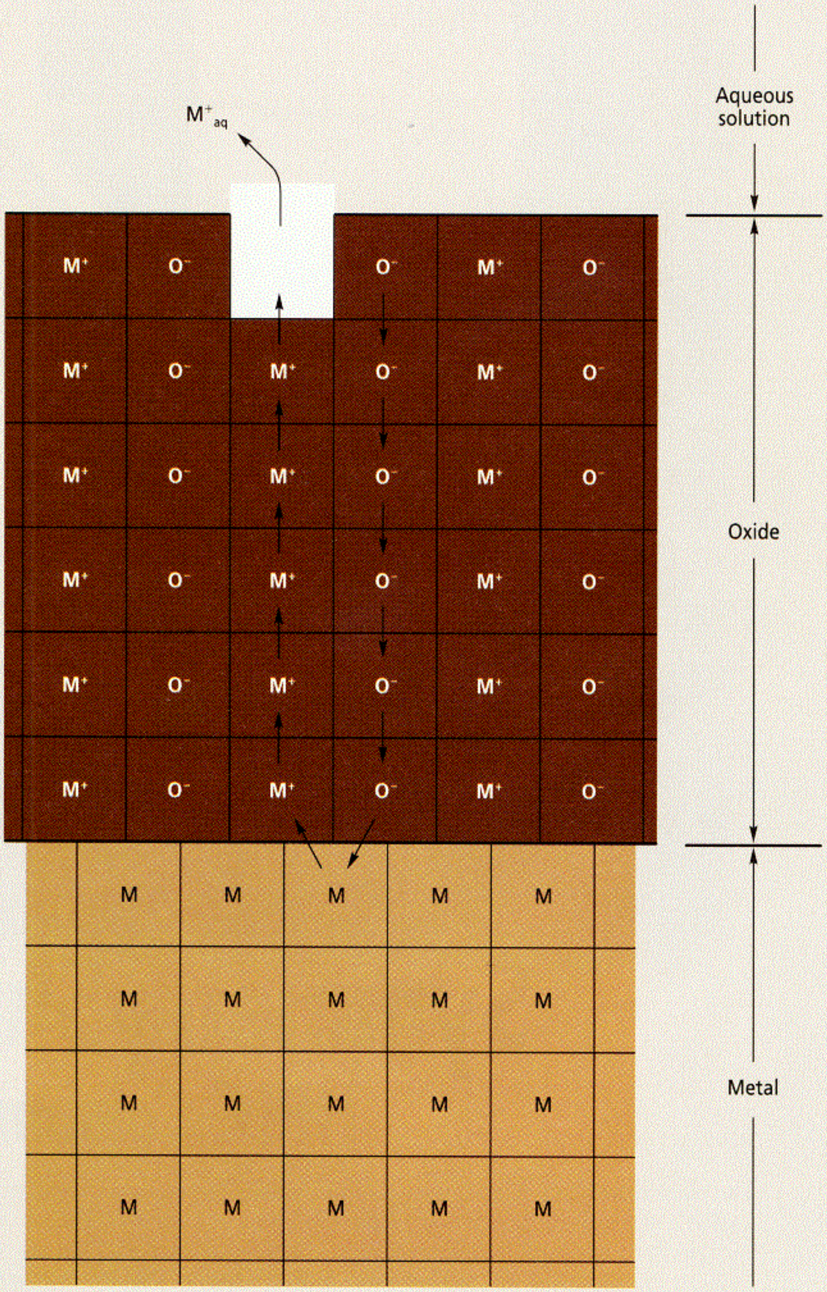

**Figure 3:** A conceptual cross-section of the oxide passivation layer showing how the diffusion of metal-ion vacancies from the top toward the bottom, oxidation of metal ($M \rightarrow M^+$) at the metal-oxide interface, and diffusion of oxide ions from the bottom toward the top leads to an overall migration of an oxide layer from the top toward the bottom of the figure.

Another type of corrosion, scarcely mentioned in the LC literature, but potentially important in special cases, is erosion corrosion. This type of corrosion occurs when a fluid such as mobile phase flows very rapidly along a solid surface. In LC the linear mobile-phase velocity is high through the frits and column packings and very high through the narrow-bore connection tubing. For a typical LC system operating at a 1-mL/min flow rate, the average flow velocity in a 0.25-mm i.d. connection tube is approximately 0.3 m/s. At this velocity, a 3% aqueous solution of sodium chloride corrodes type 316 stainless steel at a rate of approximately 0.1 μg/mm$^2$ per day (14). If a 50-cm length of 0.25-mm i.d. type 316 connection tubing is present in a mobile-phase line (surface area approximately 400 mm$^2$), this surface would corrode at a rate of approximately 40 μg per day from erosion corrosion alone. With small-bore tubing, higher flow rates as in fast LC, or elevated temperatures, this threat could be serious, even with less aggressive mobile phases. To make this threat even greater, the inner surfaces of some LC connection tubing may be extremely rough, which enables other corrosion factors such as turbulence and cavitation to contribute significantly (15).

In addition to oxide-migration corrosion, pit corrosion, and erosion corrosion, various other types of corrosion also can contribute. Most important for LC may be corrosion mechanisms based predominantly on electrochemical reactions involving microcrystalline domains that function

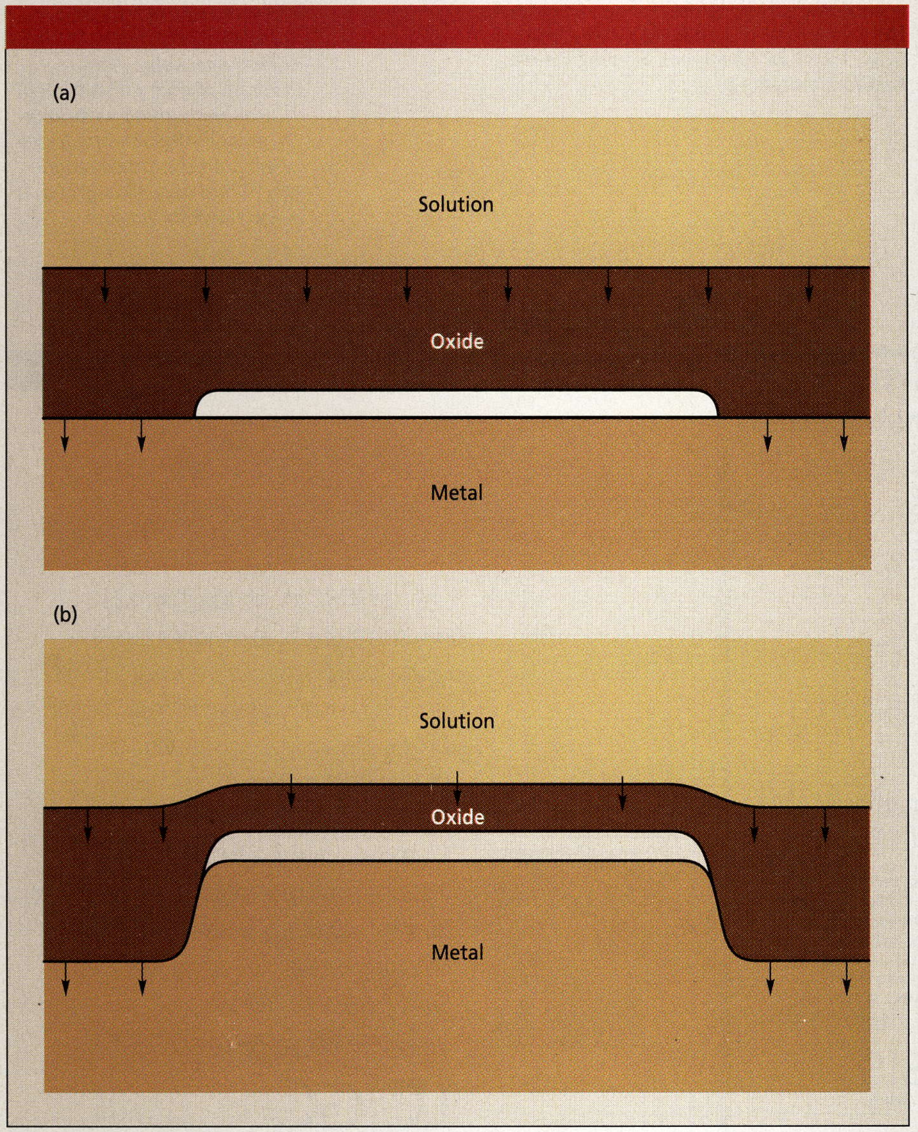

**Figure 4:** Representation of the onset of pit corrosion in which (a) an open gap forms under the oxide layer and (b) the oxide layer thins progressively before the solution attacks the underlying metal.

as microelectrodes. Interested readers should look at publications by Shoup and Bogdan (6) and Pickering (5) for more information.

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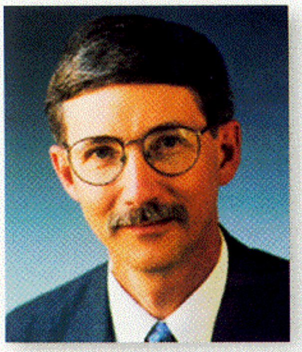

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