

Corrosive Environments

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Aqueous Corrosion Background

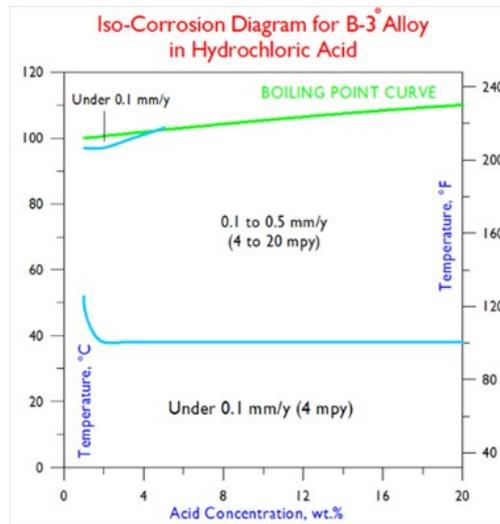
Corrosion in aqueous solutions is an electrochemical process, involving ions (electrically charged atoms) and the transfer of electrical charges at the metallic surfaces. Anodes and cathodes occur locally on the surfaces; metal is removed at the anodes (in the form of positively charged ions, i.e. $M \rightarrow M^+$). Electrons flow within the metallic material from anodic sites to cathodic sites, and vice versa in the aqueous solution. The principle cathodic reaction during corrosion by acids is the reduction of positively charged hydrogen ions to regular hydrogen atoms (i.e. $H^+ \rightarrow H$), and subsequently hydrogen molecules (gas). Hence the term reducing acid solution. An oxidizing acid solution is one that induces a cathodic reaction of higher potential; oxidizing acids tend to induce passivation (passivity), whereby protective films form on the metallic surfaces. These films can be multi-layered and can be oxides, hydroxides, or oxy-hydroxides.

The corrosion performance of even one metallic material is a very complex issue, given that there are many forms of corrosion, each dependent upon temperature, concentration, and the chemical purity of the solution. To simplify matters, therefore, this section deals with each form of corrosion in turn, with particular emphasis on the key industrial, inorganic chemicals, and upon the characteristics of each of the major alloy families (within the realm of corrosion-resistant, nickel- and cobalt-based alloys). The emphasis on inorganic chemicals is a reflection of their ionic nature, hence ability to induce an electrochemical (corrosive) process.

Uniform Corrosion in Hydrochloric Acid

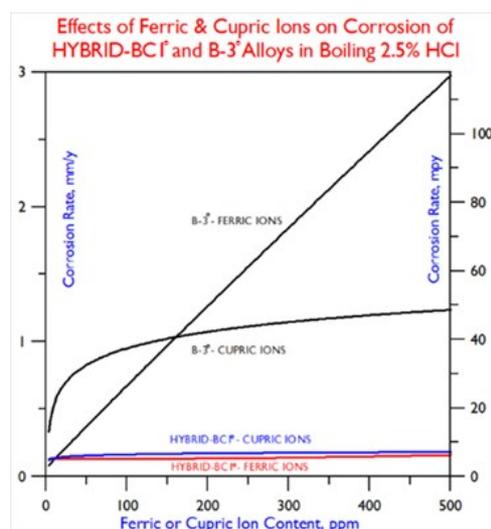
Hydrochloric is a reducing acid. It pervades the chemical processing industries (CPI), both as a feedstock and by-product. It is extremely corrosive to most metals and alloys. As will be discussed, many nickel-based corrosion alloys (particularly those with high molybdenum contents) are able to withstand pure hydrochloric acid, within specific concentration and temperature ranges. Be aware, however, that the concentration and temperature dependencies can be strong with certain alloys, and that upset conditions in industry can result in significantly higher corrosion rates when these alloys are pushed close to their limits. Furthermore, some nickel alloys, notably those in the nickel-molybdenum family, are negatively affected by the presence of oxidizing impurities (which can occur in “real world” solutions of hydrochloric acid). Industrial field trials are therefore important, prior to use.

The alloys with the highest resistance to pure hydrochloric acid are those of the nickel-molybdenum family, whose molybdenum contents are close to 30 wt.%. Within this family, the wrought material with the highest level of corrosion resistance plus thermal stability is HASTELLOY® B-3® alloy. The corrosion rates of B-3® alloy in pure, reagent-grade hydrochloric acid are shown in the figure below, as a function of concentration and temperature. Such charts (known as “Iso-Corrosion Diagrams”) will be used frequently in this manual, so some explanation is in order.



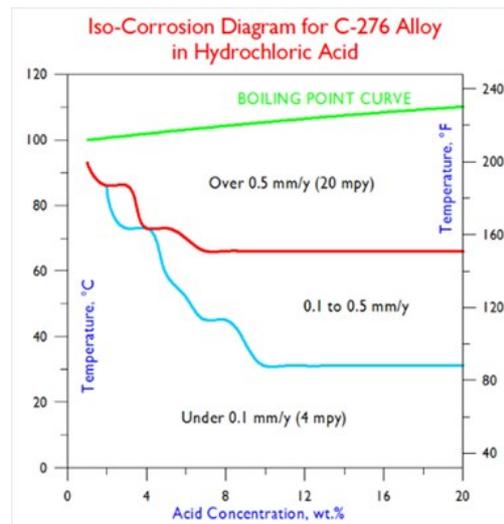
These diagrams were constructed mathematically from numerous laboratory data points, and each one defines, for a given alloy and solution, the “very safe”, “moderately safe”, and “unsafe” concentration/temperature regimes. These correspond to the corrosion rate ranges 0 to 0.1 mm/y, 0.1 to 0.5 mm/y, and over 0.5 mm/y. For those more familiar with the traditional American units (mils per year, or mpy), 0.1 mm/y is equivalent to 4 mpy, and 0.5 mm/y is equivalent to 20 mpy. It is noteworthy that, like all the materials in the nickel-molybdenum family, B-3[®] alloy is able to withstand pure hydrochloric acid at all temperatures up to the boiling point curve, within the 0 to 20 wt.% concentration range. Tests of the type used to create these diagrams (involving unpressurized glass flask/condenser systems) are only accurate in hydrochloric acid up to a concentration of 20 wt.% (the azeotrope). At higher concentrations, hydrogen chloride gas can escape, resulting in concentration instability and the possibility of erroneous results.

Below is a graph illustrating the effects of oxidizing impurities (ferric ions and cupric ions) upon the performance of B-3[®] alloy in hydrochloric acid (in this case boiling 2.5% HCl). For comparison, HASTELLOY[®] HYBRID-BC1[®] alloy, which contains 15 wt.% chromium in addition to a relatively high molybdenum level, is shown.

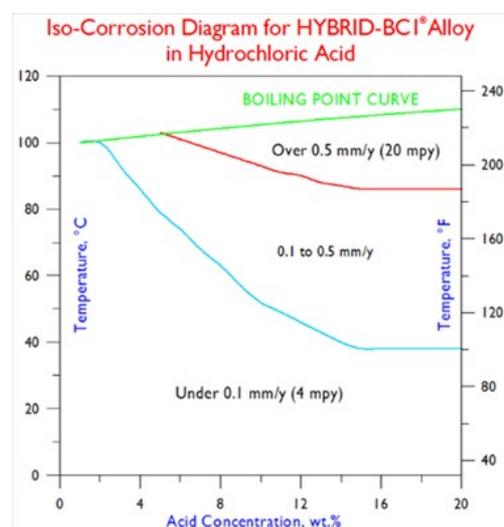


The alloys with the next highest resistance to pure hydrochloric acid are those of the nickel-chromium-molybdenum family, whose molybdenum contents range from about 13 to 22 wt.% (in some cases augmented by tungsten, which is half as effective as molybdenum on a wt.% basis). The most widely used, wrought material in this family is HASTELLOY[®] C-276 alloy, which

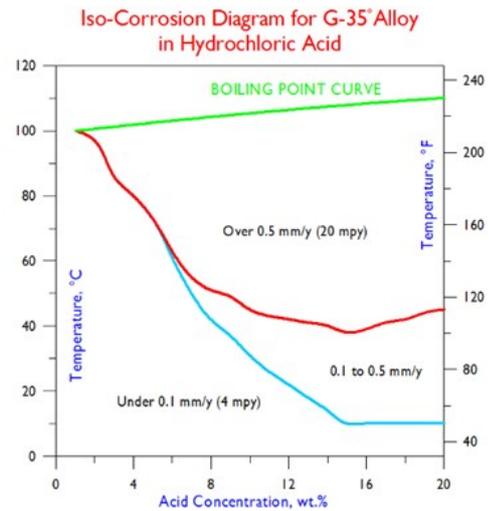
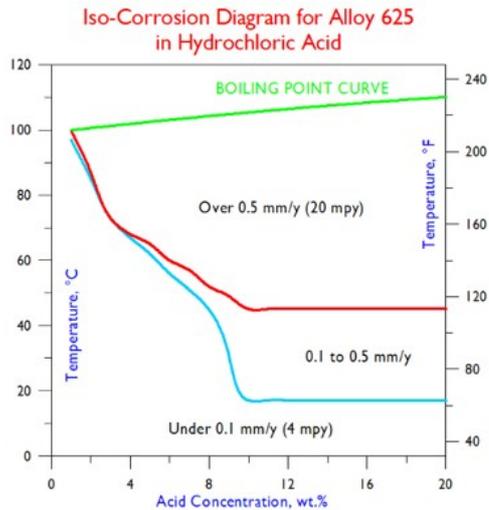
contains 16 wt.% of both chromium and molybdenum, plus 4 wt.% tungsten. Its iso-corrosion diagram for pure hydrochloric acid is shown below.



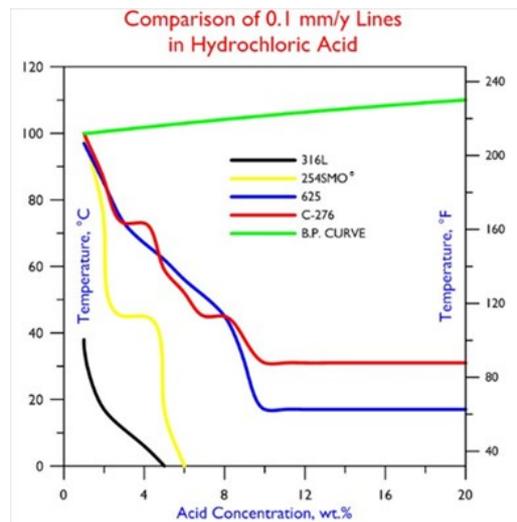
From the above diagram it is evident that the 16 wt.% molybdenum alloys exhibit strong temperature dependencies, especially at lower concentrations. The importance of molybdenum in resisting pure hydrochloric acid is illustrated in the next figure, which shows the corresponding iso-corrosion diagram for HASTELLOY® HYBRID-BC1® alloy, a material which contains 22 wt.% molybdenum (and 15 wt.% chromium, but no tungsten). Note the much broader “very safe” and “moderately safe” regimes, and generally higher temperature capabilities.



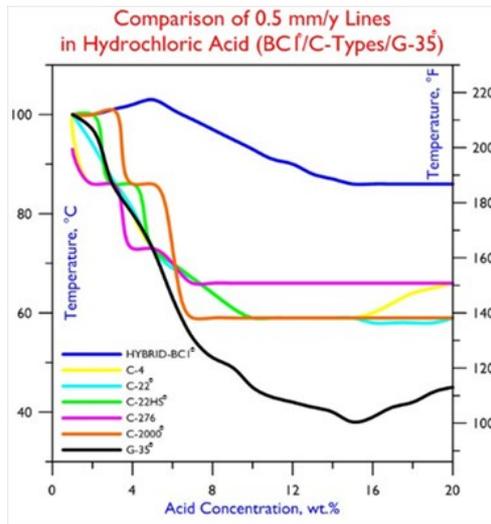
Two of the nickel-chromium alloys, namely 625 and HASTELLOY® G-35® alloy, contain sufficient molybdenum to provide good resistance to hydrochloric acid. The nominal molybdenum content of 625 alloy is 9 wt.%; that of G-35® alloy is 8.1 wt.%. The chief differences between these two materials are the chromium contents (21.5 wt.% for 625 alloy versus 33.2 wt.% for G-35® alloy) and the fact that G-35® alloy contains little else, whereas 625 alloy has deliberate iron (2.5 wt.%) and niobium (3.6 wt.%, including any associated tantalum) additions. The corresponding iso-corrosion diagrams for 625 and G-35® alloys are shown in the following two figures. The similarity of these two diagrams indicates that chromium content has little effect upon the performance of such alloys in pure hydrochloric acid.



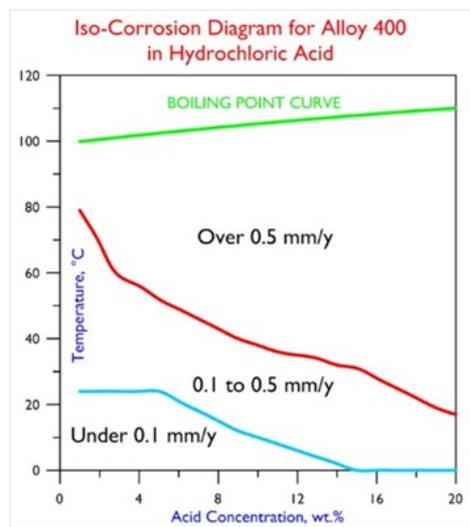
To compare materials, it is customary to plot their 0.1 mm/y lines, i.e. the lines separating the “very safe” and “moderately safe” regimes. This does not work for all materials, in particular B-3[®] alloy, which exhibits two 0.1 mm/y lines (one running horizontally at approximately 40°C), neither of which indicates that, unlike most other materials, B-3[®] alloy is safe to use up to the boiling point curve in pure hydrochloric acid, at concentrations up to 20 wt.%. Nevertheless, a comparative 0.1 mm/y line plot such as that shown below does provide perspective on the hydrochloric acid resistance of two nickel alloys (625 and C-276 alloy) versus that of two commonly used, austenitic stainless steels.



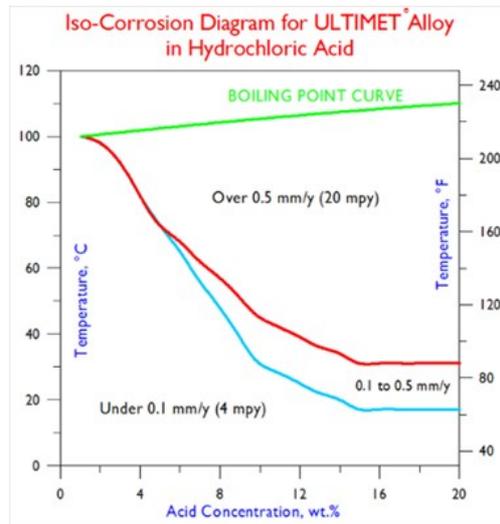
Plots of 0.5 mm/y lines can also be used to compare materials. Below is a comparative 0.5 mm/y chart for several chromium- and molybdenum-bearing, nickel-based HASTELLOY[®] alloys (including all of the versatile C-type materials), in reagent grade hydrochloric acid.



As already mentioned, copper is beneficial to the resistance of nickel alloys to reducing acids, of which hydrochloric acid is stereotypical. Hence it is relevant to present and discuss the iso-corrosion diagram for MONEL[®] 400 alloy, the most commonly used nickel-copper alloy, the nominal copper content of which is 31.5 wt.%. This diagram is shown in the following figure and indicates that, while the nickel-copper alloys possess some resistance to pure hydrochloric acid (higher than that of the common austenitic stainless steels), their performance is well below that of 625 and G-35[®] alloys (from the nickel-chromium group).



The only wrought, corrosion-resistant cobalt alloy that has been tested extensively enough in pure hydrochloric acid to enable the construction of an iso-corrosion diagram is ULTIMET[®] alloy. This is presented below. Interestingly, despite its relatively low molybdenum and tungsten contents (5 and 2 wt.%, which are equivalent to 6 wt.% molybdenum), its performance in pure hydrochloric acid bears some resemblance to that of 625 and G-35[®] alloys. The main difference is the narrower “moderately safe” regime at concentrations in the range 10 to 20 wt.%, indicating that it transitions from “safe” to “unsafe” over a smaller temperature range.



Uniform Corrosion in Sulfuric Acid

Sulfuric acid is also a very important and very corrosive industrial chemical. It is used in the manufacture of fertilizers, detergents, plastics, synthetic fibers, and pigments. It is also used as a catalyst in the petroleum industry. As with hydrochloric acid, the concentration and temperature dependencies can be strong for certain nickel- and cobalt-based materials. Also, “real world” conditions (in terms of chemical purity and flow) are unlike those in the laboratory used to generate the data in the following diagrams, so field trials are recommended. In pure sulfuric acid, again molybdenum is highly beneficial; copper is also advantageous.

Although the high-molybdenum alloys perform well across the whole concentration range in pure sulfuric acid, this is despite the fact that the nature of the cathodic reaction changes for many metallic materials at a concentration of approximately 60 to 70 wt.% (*Sridhar, 1987*). At lower concentrations, the cathodic reaction is believed to be the reduction of positively charged hydrogen ions (and the evolution of hydrogen gas), whereas mixed cathodic reactions appear to be in play at high concentrations. This affects the behavior of metallic materials such as the zirconium alloys and nickel-copper alloys.

As with pure hydrochloric acid, the nickel alloys with the highest resistance to pure sulfuric acid are those of the nickel- molybdenum family, as indicated in the following iso-corrosion diagram