Iron Solubility in Sulfuric Acid

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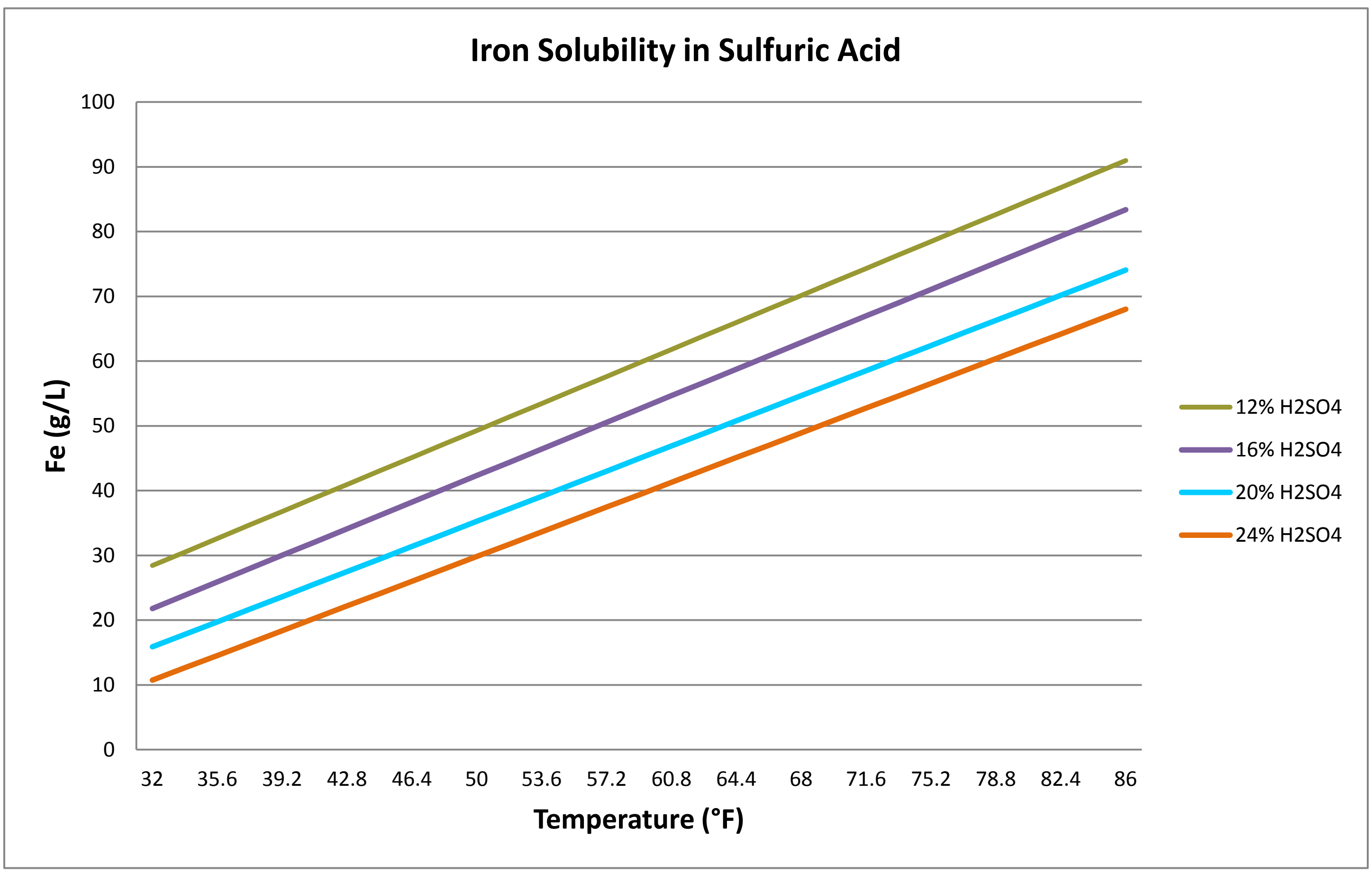
The solubility of iron in sulfuric acid solution is controlled by several variables. The most common and dominant influences on iron's ability to stay in solution are temperature and acid concentration. The manipulation of these two interacting forces can result in either an excellent quality, clean pickling solution or a spent volume of highly contaminated solution that ruins the product.

I. Temperature

As shown on the chart, the **temperature** of the pickling solution greatly affects the ability of iron to stay in solution. As heat is removed from iron saturated pickling solutions, the supersaturated iron forms a crystalline solid known as ferrous sulfate heptahydrate and precipitates from solution. As the temperature of the acid solution decreases from normal pickling temperature (113°F – 167°F) to 41°F, the iron continues to drop out at a near linear rate. This heat removal principle is the basis of acid recovery. Beta coined the term *freeze crystallization* to reflect this process. The pickling industry refers to systems that do this as *crystallizers*.

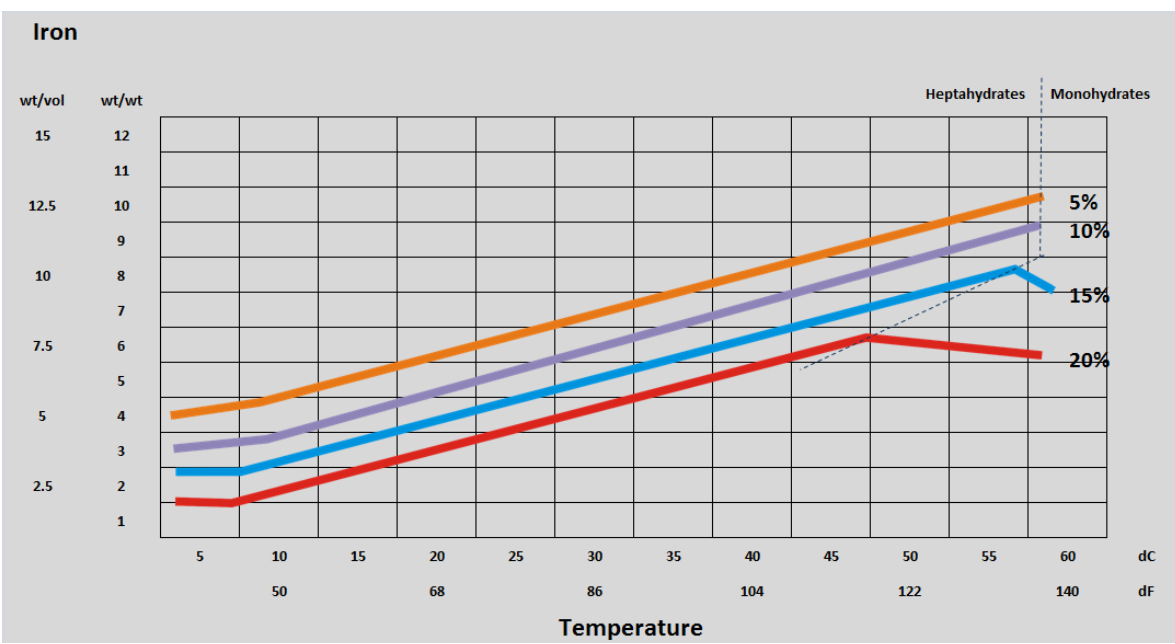


At a temperature of 41°F, almost 90% of the iron that can cost effectively be removed by refrigeration has crystallized. On a cost-engineering basis, processing more volume with 90% efficiency is more cost effective than attempting removal of the final 10% at a greatly increased capital and operating cost. Since other forces such as agitation and chemical additives also interfere with the removal of the final 10%, chasing this fractional percent of iron removal in dynamic pickling operations becomes impractical.

II. Acid Concentration

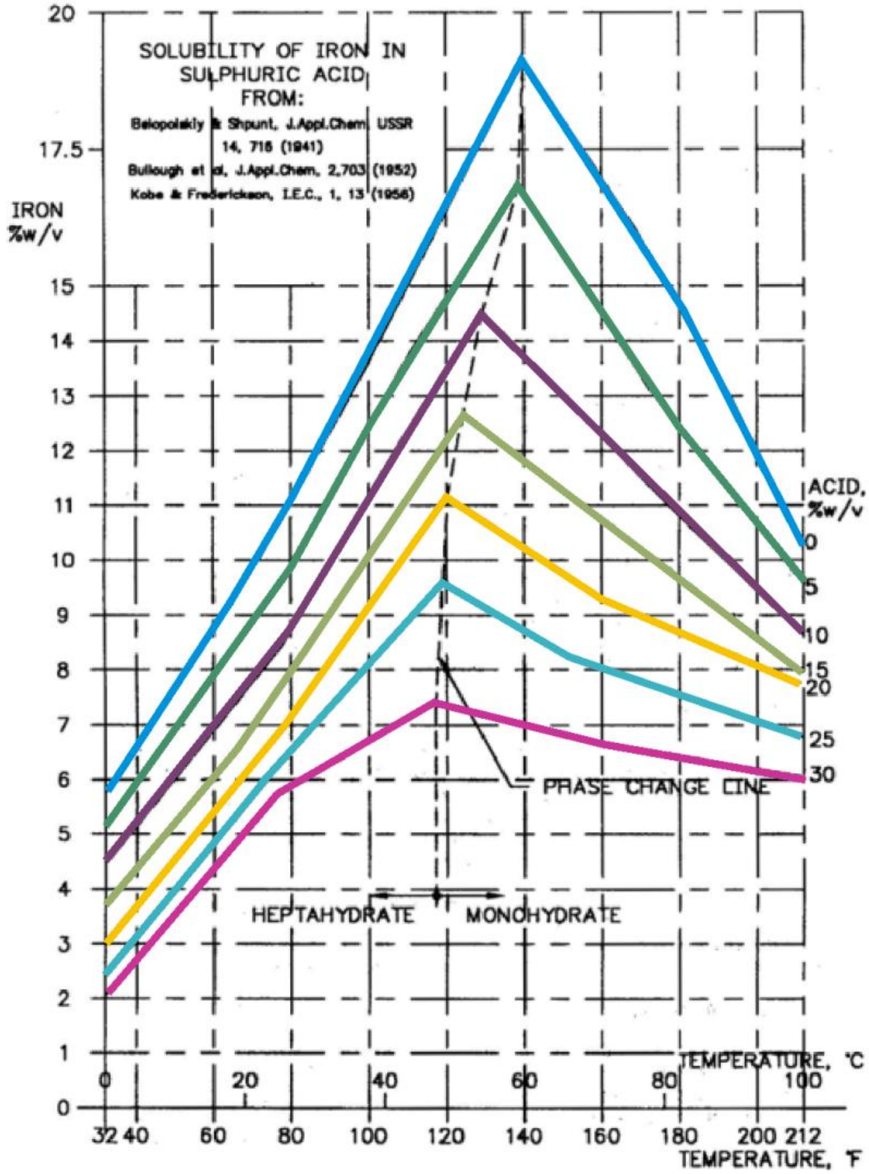
The second important variable to consider when crystallizing iron from sulfuric acid solution is **acid concentration**. An excess of sulfuric acid is necessary to effectively build the crystals. The more that excess sulfates are available, the more readily the crystals are formed. This *common-ion effect* follows Le Chatelier's principle of Chemistry—in a solution at equilibrium (Fe saturation) any change in temperature or concentration will force change. If we add concentrated H_2SO_4 to the pickling solution, we will force the $FeSO_4$ to drop out of solution. Hydrogen is much more soluble than iron, so Fe is forced out of solution until homeostasis has returned.

In the chart below, the relationship of different acid concentrations is displayed. Translating this chart into pickling practice shows that a 10% concentration of sulfuric acid at about 140°F is ideal for most picklers. (Concentrations of up to 24% are also used to speed pickling and for special alloys.) The speed of pickling is excellent and the solubility of iron is highest without creating ferrous sulfate monohydrate. Most steel picklers like to operate their pickling bath with an Fe concentration below 7% wt/wt and with a Sulfuric Acid concentration between 8% and 14% wt/wt. Picklers with acid recovery systems like to maintain their baths at 5% Fe ± 1%. To optimize the speed of pickling and avoid the formation of hard, thick buildups of Ferrous Sulfate Monohydrate crystals on their heat exchangers, the typical pickler with an acid recovery system will operate between 113°F and 140°F.



III. Other Factors Influencing Solubility

Although temperature and acidity remain the greatest factors influencing iron solubility, there are several other factors affecting pickling solutions. Agitation, other metals, and chemical additives often alter the solubility of iron in solution and pickling efficiency. These factors, combined with acid addition procedures and acid bath heating methods, often cause the pickling bath to wander from ideal chemistry.



Tank agitation (or lack of) causes variance from the solubility curves. If the tank is air agitated away from the heating source, iron crystals may form in the tank due to zone cooling. This can coat both the immersed metal and the bottom of the tank with a layer of crystals. The better practice is to keep the bath moving, especially around the heat exchanger. If the exchanger does not see good movement, the excessively high-temperature around the exchanger will exceed the solubility limit of the heptahydrate crystal formation and begin to generate the Ferrous Sulfate Monohydrate crystals on and around the high-temperature zone. The generation of the monohydrate crystals eventually retards the performance of the heat exchanger and deposits the white crystals on the product. The curve above illustrates the effect of both temperature and iron concentration in the pickling operation.

This *zone concentration* phenomenon is also true for concentrated acid additions. In like manner, if excessive volumes of concentrated acid are introduced into a tank very quickly, the acid concentration in that zone may cause precipitation of monohydrate crystals. (See La Chatelier's principle.) To prevent this, introduce *raw* acid by slowly dispersing the raw acid into different areas of an agitated tank.

Metals besides iron are often dissolved into the pickling bath. Zinc is commonly dissolved along with the iron when galvanized products are stripped for reprocessing or brought into the bath on racks and hooks. Fortunately, zinc forms a heptahydrate crystal similar to iron and will precipitate along with the iron in the acid recovery system. Chrome, Nickel, Manganese, and other metals appear in solution when alloys are pickled. These metals may eventually build up to inhibit pickling. In most cases there is little impact, but in the stainless steel group the accumulation of the non-ferrous metals can eventually cause stains on the product. Although these stains can be rinsed or etched off, the background metals should be monitored. Eventually the bath will require dumping.

Chemicals such as acid extenders, wetting agents, and fume suppressors change the solubility curve slightly. When excessive, they can cause problems in the equipment used to recover the acid. Wetting agents are typically used to allow quick draining of the product as it emerges from the pickling tank. They change the viscosity, surface tension, and/or flowability of the solution. Excessive amounts of wetting agents affect the removal of iron from the acid solution by interfering with crystal matrix formation, thus creating smaller crystals. Like inhibitors, the wetting agents need to be carefully dosed and tested regularly to insure good performance.

Fume suppressors are added to acid to improve conditions in the workplace. Heated, concentrated acid can emit noxious gas detrimental to the production workers as well as the equipment and facility. The fume suppressors change the surface of the acid to greatly reduce gas evolution. When overdosed, fume suppressors (and sometimes wetting agents) create suds in acid recovery equipment. Since the chilling vessel agitators in acid recovery equipment provide violent stirring to optimize heat exchange, they also promote the generation of foam. The foam traps crystals in solution and brings them to the surface. The equipment becomes incapable of settling the crystals for separation in a centrifuge. The trapped crystals eventually float into the clarified acid returning to the pickling bath and are re-dissolved as the acid is reheated. This severely reduces the efficiency of the system and can entrain solids that get into the tube and shell heat exchangers. Normal and proper doses of the wetting agents and fume suppressors will not impact acid recovery.

IV. Conclusion

The chemistry involved with pickling is not an art form, nor is it black magic. Once the chemistry is controlled, the process becomes repeatable and manageable. No matter which acid concentration or operating temperature the pickler chooses, the solubility curves will predict the results. Acid recovery will help maintain predictable and reliable chemistry and meet environmental goals.

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