Troubleshooting Guidelines

American Galvanizers Association (720) 361-4485 technical@galvanizeit.org

PROBLEM: Measuring & Adjusting pH of the Preflux Solution

Why is Maintaining the pH of the Preflux Solution Important?

After hydrochloric (HCl) or sulfuric (H_2SO_4) acid pickling, acid and dissolved iron are carried over into a zinc ammonium chloride preflux solution. If the preflux solution becomes too acidic, the ability of the preflux solution to provide oxidation protection for the steel products is reduced and may lead to uncoated areas (bare spots) during galvanizing. A low pH will also increase corrosion of heating coils and increase the amount of soluble iron in the preflux bath, leading to increased dross formation in the galvanizing kettle. Additionally, if the pickle acid is sulfuric, the flux bath can also become contaminated with sulfates which can interfere with proper flux activity. If the pH of the preflux bath is too high, decomposition of zinc chloride in the preflux solution will occur, decreasing the effectiveness and preventing adequate drying of the steel after removal from the preflux tank. Variation in pH can also impact the efficiency of flux filtration systems.

What is the Optimal pH Value for the Preflux Solution?

For heated zinc ammonium chloride preflux solutions, the pH should not fall below 3.5 and should be maintained between 4.0-4.5 for optimal performance. At this pH range, normal agitation of the solution by moving work through the tank is enough to convert the dissolved iron into a sludge which will settle at the bottom of the tank, minimizing the effect of iron on both preflux performance and dross formation. It is also optimal to maintain this pH range for easier removal of impurities (iron, sulfates) from the preflux solution during maintenance.

Measuring pH of the Preflux Solution

The pH of a solution can be easily measured at the galvanizing plant by sampling and the use of a universal indicator solution, portable pH meter, or pH indicator paper.

For preflux baths, the recorded pH value using standard methods is only an approximate number and should be considered accurate within 1 unit of the pH read. The presence of iron or other salts can interfere with indicators, the pH probe, or the color formed on indicator strips, leading to inaccurate results at pH values which are typical of preflux solutions. As a result, pH measurements by standard methods should only be utilized for monitoring and making adjustments once a sample has been sent to an accredited laboratory testing to achieve an accurate pH value. A laboratory test value should be acquired each time a new flux solution is generated. Once the true pH is provided by an accredited laboratory, compare with the results taken at the galvanizing plant to determine the amount to adjust all pH readings for use in calculations. See **Example 1** at the end of this guideline for an explanation of adjusting pH readings.

Be sure to agitate the preflux to ensure samples are taken from a uniform solution and from several different bath locations. The pH of the preflux solution will vary with temperature, so all measurements must be performed at the same temperature to ensure consistent results (preferably at room temperature).

Adjusting pH of the Flux Solution

To increase preflux pH, add ammonium hydroxide (NH_4OH), also referred to as aqueous ammonia ($NH_{3(aq)}$). The pH can also be increased slowly by placing zinc slabs and preflux product into the tank at a ratio recommended by the preflux supplier. However, the repeated use of this method for pH control tends to produce a build-up of impurities requiring additional maintenance.

To decrease preflux pH, add a hydrochloric acid solution. To prevent contamination, pH should never be adjusted using sulfuric acid or acid/caustic rinse waters.

To determine the minimum amount of ammonium hydroxide solution or hydrochloric acid solution required to achieve target pH values, see the attached **Examples 2 and 3** at the end of this guideline for example calculations. If using zinc slabs to increase preflux pH, consult the preflux supplier to acquire the recommended ratio of preflux product to add with the zinc. As a shortcut, the AGA Technical Department or the preflux supplier can help to develop a table specific to the galvanizing plant based on tank size, preflux product, and acid strengths. Such tables identify the minimum additions required to adjust the pH level from various initial readings so that detailed calculations do not need to be regularly performed by operations personnel or in-plant chemists.

It is important to note that tables or any calculations should only be used to estimate the *minimum* amount of hydrochloric acid, ammonium hydroxide, or zinc/preflux required to achieve the desired pH. Salts contained within the flux bath will cause a buffering effect, so final adjustments should be made slowly based on experience and confirmed by sampling of the bath to test for pH. Additionally, when using any of the prescribed methods to adjust preflux pH, there exists the opportunity to negatively affect the ratio of the system, which may necessitate further adjustments.

During adjustments, ensure the preflux solution is well agitated and that the addition of any solution is distributed to several points around the tank. This process ensures even distribution and prevents settling.

To minimize the frequency of pH adjustments required, rinse steel articles very well after pickling to minimize acid carry-over. Rinsing performance is typically improved by vigorous agitation in the rinse tank, using two static rinsing tanks after pickling, or spraying water on parts coming out of the rinse tank.

Example 1: Adjustment of pH Readings for Preflux Solutions

3.5 = pH value determined at the galvanizing plant (erroneous reference pH)
4.0 = pH value obtained from an accredited laboratory (true pH)

In this example, all measurements performed by the galvanizer should be adjusted by +0.5 to achieve true pH readings. If the galvanizer samples the preflux solution and records a reference pH of 2.5, this means the true initial pH value is 3.0. After maintenance is performed to increase the preflux solution to a true pH of 4.0-4.5, the galvanizer should adjust for the discrepancy and work to achieve a reference pH between 3.5-4.0.

Example 2: Amount of Hydrochloric Acid (HCl) Solution to Decrease Preflux pH

For a preflux tank with a bath volume of $28m^3$, determine the amount of 37% hydrochloric acid stock solution ([HCl] = 12 mol/L) required to lower the pH of the preflux solution from a true initial value of 6 to a target pH of 5.

To determine how much hydrochloric acid must be added to the preflux tank, the galvanizer will need to collect the following information:

- True Initial pH of the preflux tank, **$pH_{initial}$ = 6**
- Target pH for the flux tank, **pH_{target} = 5**
- Concentration of hydrochloric acid in (moles/Liter), **[HCl] = 12 mol/Liter**
  Note: Assumes 37% stock solution, but galvanizer can utilize any solution type. Molarity will vary with solution concentration.
- Volume of liquid in the preflux tank in Liters, **V_{tank}, = 28,000 Liters**
  Note: Volume = L*W *H of the liquid in meters, and 1 cubic meter = 1000 Liters

Then solve for the minimum volume of hydrochloric acid (HCl) required:

$$Voume_{HCl} = \frac{(10^{-pH_{target}} - 10^{-pH_{initial}}) * V_{tank}}{[HCl] - 10^{-pH_{target}}}$$

$$Voume_{HCl} = \frac{(10^{-5} - 10^{-6}) * 28000}{12 - 10^{-5}} = 0.0210\ Liters\ or\ 21.0\ mililiters$$

Note: This calculation should only be used to estimate the minimum amount of hydrochloric acid required to achieve the desired pH. Salts contained within the flux bath will cause a buffering effect, so final adjustments can be made based on experience and confirmed by sampling of the bath to test for pH.

Example 3: Amount of Ammonium Hydroxide (NH_4OH) or Aqueous Ammonia ($NH_{3(aq)}$) Solution to Increase Preflux pH

For a preflux tank with a bath volume of 28m^3, determine the amount of 56.5% ammonium hydroxide solution ([NH_4OH] = 14.5 mol/Liter) required to raise the pH of the preflux solution from a true initial value of 3.5 to a target pH of 4.5.

To determine how much ammonium hydroxide solution must be added to the preflux tank, the galvanizer will need to collect the following information:

- True Initial pH of the preflux tank, **$pH_{initial}$ = 4.0**
- Target pH for the flux tank, **pH_{target} = 4.5**
- Concentration of ammonium hydroxide in moles/Liter, **[NH_4OH] = 14.5 mol/L**. **Note:** Assumes 56.5% stock solution, but galvanizer can utilize any solution type. Molarity will vary with solution concentration.
- Volume of liquid in the preflux tank in Liters, **V_{tank}, = 28,000 Liters**
  Note: Volume = L*W *H of the liquid in meters, and 1 cubic meter = 1000 Liters

First solve for the concentration of free hydroxide ions, **[OH^-]** using the known concentration of the ammonium hydroxide solution:

$$[OH^-] = \sqrt{1.78 \times 10^{-5} * [NH_4OH]} = \sqrt{1.78 \times 10^{-5} * 14.5} = 0.0161\, mol/Liter$$

Then use the above value for [OH^-] to solve for the minimum volume of ammonium hydroxide solution required:

$$Volume_{NH_4OH} = \frac{(10^{-pH_{initial}} - 10^{-pH_{target}}) * V_{tank}}{10^{-pH_{target}} - [OH^-]}$$

$$Volume_{NH_4OH}\ \frac{(10^{-4.0} - 10^{-4.5}) * 28000}{10^{-4.5} + 0.0161} = 119\ Liters$$

Note: This calculation should only be used to estimate the minimum amount of ammonium hydroxide required to achieve the desired pH. Salts contained within the flux bath will cause a buffering effect, so final adjustments can be made based on experience and confirmed by sampling of the bath to test for pH.