# On-Site Testing of a New Process for Recycling Galvanizing Flux Solution

by:
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**Continuous microfiltration and oxidation removes iron and suspended solids from working flux tanks.**

Given a wire plant's daily focus on production, there is little time to notice the creep of deteriorating chemistry in the flux. And yet, like unchecked mold and debt, it will eventually overwhelm you. This case study follows a new process for continuously maintaining excellent flux chemistry and examines the financial ramifications.

## The Problem

Continuous drag-in of iron contaminants eventually renders the flux solution unsuitable for further galvanizing. The iron contamination is often found to be responsible for thicker zinc coatings, increased skimmings and dross, black/bare spots and other cosmetic degradation.

## Effect of Iron Contamination

To quantify the negative effects of a contaminated flux tank, flux data was collected from selected galvanizers over several years. The increase in $Fe^{+2}$ (ferrous) from a fresh tank until it was dumped with nearly 0.6% Fe was tracked against the percentage of Gross Zinc Usage (GZU) and skimmings. **Figure 1** shows general trends, using averages of participating galvanizers (data from Dr. Tom Cook, *finishing.com*, Sept. 30).

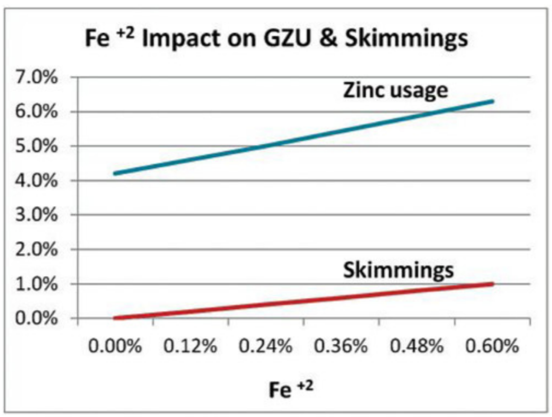



**Fig. 1 — Impact of iron contamination in flux tanks.**

Assuming a zinc cost of US$1.47/lb, then every 1% excess Zn coating will cost approximately US$ 14,700 per million pounds of galvanizing.

## Flux Treatment Options

Batch chemical treatment and bulk disposal are the most common contaminated flux handling choices. Frequent disposal of contaminated flux, however, is very expensive. Chemical batch treatment to remove contaminants requires time, labor, equipment, chemicals to convert the insoluble iron contaminants into filterable solids and dead-end filters to remove the solids.

The *Crossflow Microfiltration process that employs ozone oxidation of iron contaminants* offers a new approach to continuously remove contaminants without the complexities of batch treatment. *Crossflow microfiltration membranes* are the key to this cleaner, less invasive alternative. In crossflow microfiltration, a dirty, solids-laden solution is pumped at high velocity through the inner surface of the porous tubular membranes. The velocity of the solution scours the surface to discourage thick deposition of the solids onto the membrane surface. As the solids flow through, the *Permeate* (solids-free solution) migrates through the walls of the membranes.

As seen in **Figure 2**, applying crossflow microfiltration membranes to clean a contaminated flux tank requires significantly fewer moving parts than a conventional chemical batch treatment option. While both treatment options require conversion of the soluble iron into filterable solids, the OxyFilter uses ozone to generate insoluble, filterable iron. This negates the need to meter large volumes of hydrogen peroxide that creates sludge and murky flux.

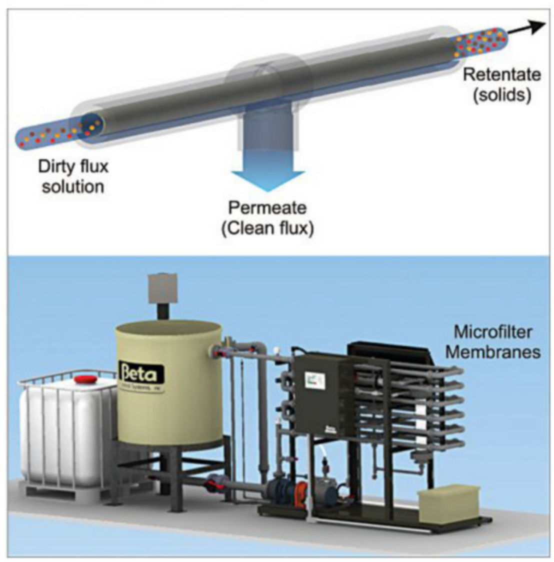
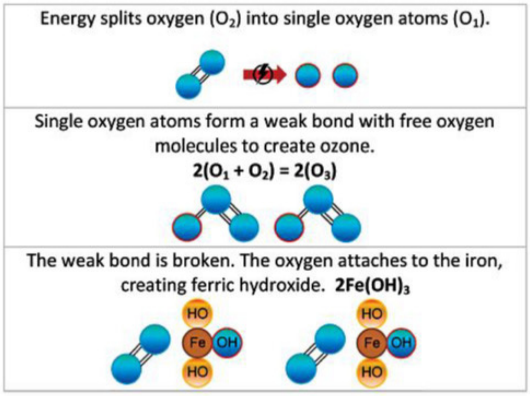



**Fig. 2 — OxyFilter using crossflow microfiltration membranes.**

## Oxidation With Ozone

Ozone ($O_3$) is a form of oxygen that has one more oxygen atom than the oxygen ($O_2$) we breathe. This highly oxidative ozone reacts with the ferrous ion ($Fe^{+2}$) to create the ferric ion ($Fe^{+3}$).


$2FeCl_2 + 2O_3 + \rightarrow 2Fe(OH)_3 + 4\,Cl^-$




At the normal pH range of flux, an insoluble ferric tri-hydroxide molecule forms to create an orange, filterable solid. Since ozone has a fairly short half-life, any excess ozone from the reaction quickly degrades to oxygen.

Ozone is the only common oxidizing agent that can be manufactured easily and inexpensively at the point of use. Ozone generators compress ambient air, remove its nitrogen to increase the oxygen concentration, and expose the oxygen to a high-voltage spark to create ozone. It is a simple process that has been used worldwide for water disinfection and purification for more than 120 years.

To test the efficiency of ozone, flux from a working galvanizing process was pumped into the OxyFilter. A known mass of ozone was reacted with a known mass of ferrous ions during this 150 minute experiment. **Figure 3** shows the declining concentration of ferrous ions as they are converted to Ferric Hydroxide. The ozone oxidized the ferrous ions to the ferric form at a nearly stoichiometric rate (97% effective) at a pH of 4. Almost all of the ferrous ions were converted from the initial 275 ppm to a level of 6 ppm. No ozone off-gas was detected.

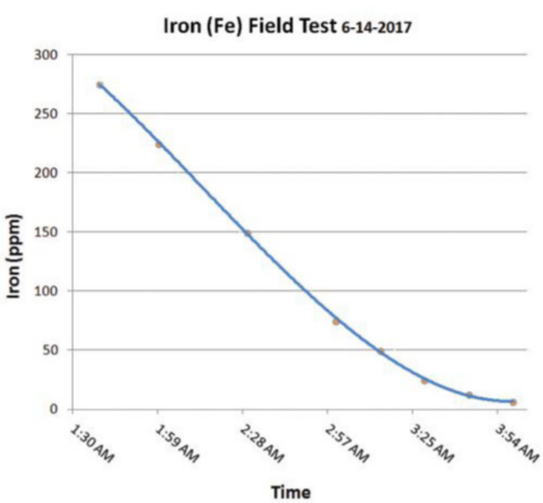



**Fig. 3 — Effectiveness of ozone on ferrous ion conversion to ferric hydroxide solids.**

## How Does the Oxyfilter Work?

The Oxyfilter works as seen in **Figure 4**.

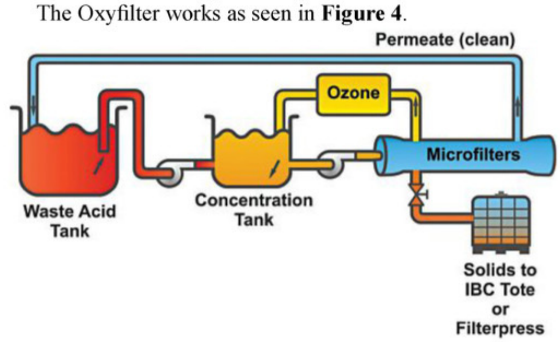



**Fig. 4 — Flow diagram - OxyFilter.**

***Step 1. Flux Tank***

First, the proper pH is maintained in the Flux Tank between 4 and 4.5. Although the OxyFilter will not be affected by pH variation, it is imperative that flux chemistry be maintained within proper parameters to insure quality galvanizing. Once the flux chemistry is correct, the system is turned on and the feed pump draws the flux into the Concentration Tank.

***Step 2. Concentration Tank***

In the Concentration Tank, soluble Ferrous ($Fe^{+2}$) ions are converted to insoluble ferric ($Fe^{+3}$) tri-hydroxide solids using ozone gas. Beta developed a patent pending process to utilize over 95% of the available ozone to remove the flux contaminants.

***Step 3. Microfilters***

After the pre-treatment, the flux is pumped at a high velocity tangentially across the surface of crossflow microfiltration membranes. The suspended solids travel quickly through the membranes and then return to the Concentration Tank. The solids-free flux solution permeates the membranes and returns to the Flux Tank with reduced iron and zero solids (see **Figure 5**).

At fifteen minute intervals, a small quantity of clean flux solution is driven backward across the surface of the membranes to clear any solids that may have built up. This "backflush" process is automatic.

***Step 4. Solids Handling***

For plants with relatively clean flux tanks, an IBC tote will handle all solids discharged when the Microfilters are backwashed. The solids will settle to the bottom of the tote while the supernatant can be decanted back into the OxyFilter. For plants with more contaminated flux tanks, a small Clarifier Tank and Filter Press can efficiently handle the solids.


**Fig. 5 — Entering and exiting flux.**

**Continued...**

## Case Study

A pilot OxyFilter (**Figure 6**) was installed on the flux tank of a general galvanizer for three months. The process was programmed to start with the push of one button. A PLC was used to run the system automatically and record operating data. The OxyFilter was untouched other than for daily sample removal.

**Fig. 6 — Pilot OxyFilter system.**

The specially made microfiltration membrane we chose for the system allows both zinc and ammonium chloride to pass through the PVDF material while rejecting solids over one micron. The material allows a full spectrum of pH ranging from high acid to high caustic values. The membrane withstands temperatures up to 190°F. For the case study, we targeted a "flux" rate of 300 GFD (gallons/square foot/day).

Performance data was collected during multiple test runs to establish both the expected permeate "flux" rate of the membranes over time and the impact of the chemical reactions on the flux solution.

Data from monthly analysis is the basis of the table in **Figure 7**. The galvanizer's rate of iron carryover is based on two rinse tanks and good rinse practices. The 5% sludge reflects solution concentration as it is removed from the OxyFilter system. The 45% reflects the solids level after decantation.

| Galvanizing Data | | |
|---|---|---|
| | Metric | US |
| Production | 90 tonnes/day | 200,000 lbs/day |
| Steel fluxed | 90,700 kg/day | 200,000 lbs/day |
| Iron (Fe) in Flux | 3.5 kg/day | 7.72 lbs/day |
| Iron (Fe) in Flux | 0.1458 kg/hr | 0.3214 lbs/hr |
| | | |
| **Projected for OxyFilter** | | |
| Ozone ($O_3$) demand | 62.6 grams/hr | 0.138 lbs/hr |
| 5% sludge | 70 kg/day | 154 lbs/day |
| 45% sludge | 7.77 kg/day | 17.13 lbs/day |

**Fig. 7 — Data from monthly analysis.**

## Results

Data from the second month's trial is seen in **Figure 8**. The pump feed rate was maintained between 8 and 10 fps

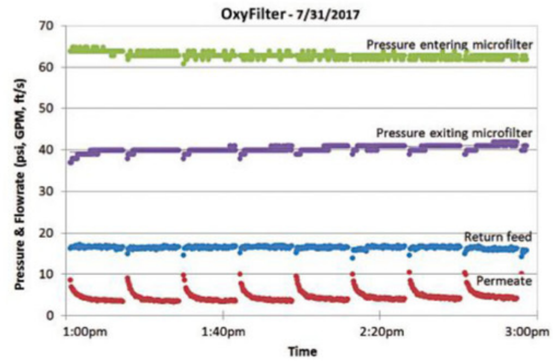



**Fig. 8 — Data from the OxyFilter system during the second month of the trial (Pump set to 50+ Hz).**

across the membrane surface. This practice allows the high velocity solution to scrub the membrane surface rather than allow solids deposition on the membranes.

**Figure 9** shows that in the early hours of run time, the permeation rate through the membranes was well above expectations.

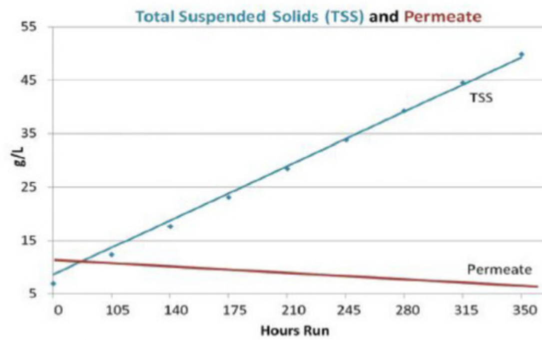



**Fig. 9 — Total suspended solids and permeate passing through membrane (Velocity = 10 fps).**

The "flux" rate slowed over the 300 to 350 hour cycle as expected. At this point, the membranes are "cleaned in place" with five gallons of 5% HCl to restore the original flux rate. **Figure 10** shows the effect of the cleaning cycle on flow rate.

Over the 300 to 350 hour cycle between start up and membrane cleaning, the ferric hydroxide solids accumulate

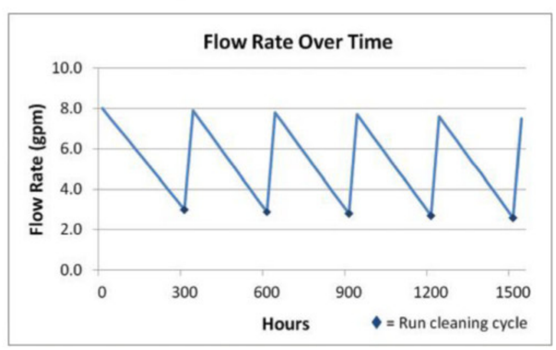



**Fig. 10 — Effect of cleaning cycle on flow.**

in the Concentration Tank. The solids are drained into an IBC tote intermittently as the solids level reaches about 50 grams per liter (5%).

## Cost Analysis

***Material Costs***—Microfiltration membranes on the Oxyfilter include a 36 month warranty, with an approximate life span of three to five years. Other replacement materials include: hydrochloric acid, pump seals and diaphragm pump replacement parts.

***Labor Costs***—Daily operation entails turning the system on/off, draining TSS from the concentration tank, testing pH and adjusting the flux chemistry if needed. These tasks take 20 minutes.

***Every Week***—Shut down the system for four hours while five gallons of 5% HCl flushes through the membranes to restore original performance. The leachate from this cleaning is simply added back into the flux tank. Hands on time = 20 minutes, Inactive time = four hours.

***Utilities***—Electricity consumption was measured at 4.5 kw.

## Summary

The trial succeeded in proving the effectiveness of both ozone, as an excellent method of converting dissolved iron into a filterable suspended solid, and crossflow microfiltration to continually remove flux contaminants. Several design modifications and mechanical changes throughout the trial allowed easier operation and maintenance. Challenges like foam suppression, drip leaks and software revisions were overcome. Further trials are now underway to "Beta" test the first product launch. *www.betacontrol.com* WCTI

***Company Profile:***

***Beta Control Systems, Inc.*** *was founded in 1980 as an environmental research and development corporation focused on providing state-of-the-art technology to the metal finishing industry. The company has installed over 150 resource recovery systems, making Beta Control Systems the worldwide industry leader with the largest number of acid recovery installations.*

*Beta acid recovery systems offer customers the benefit of minimal hazardous waste discharge. The company designs, manufactures and installs its own systems, including acid recovery (HCl, $H_2SO_4$, HF, $HNO_3$), rinse water recovery and water processing, and solids neutralization & filtration systems.*

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