

On-site Testing of a New Process for Cleaning Galvanizing Flux Solution

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Abstract

A new, patented process removes iron from working flux tanks using continuous membrane separation without requiring liquid chemicals. The paper will explain this novel process and show several months of test results on an active flux tank. Using only small quantities of electricity and compressed air, the process removes contaminants from the flux.

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1.0 Introduction

When racks of parts rise from the rinse and travel to the flux tank, they drip water with varying concentrations of iron and other contaminants from both the rinse tank and the make-up water supply. For the purpose of this paper, we will not address rinse practices or the impact of using hard water for rinse water makeup. This narrative will focus on what can be done to keep flux chemistry at optimum efficiency through a chemical/mechanical treatment and filtering process.

Over the past 38 years of visits to galvanizing plants on six continents, we have only visited one plant that had rinse practices so good that they never had to replace the flux bath. This plant had a filter to remove the orange Ferric Hydroxide solids that accumulated during normal operations, but the Ferrous and Sulfate concentrations in solution remained below 0.1% contamination levels. Due to the focus on excellent chemistry, this plant maintained a gross zinc usage (GZU) between 4 and 4.8% for most of its 20 years in service. Their dross and skimmings records paralleled this excellent result.

And then there is everybody else.

Tonnage through the plant is King. The daily focus remains on production and its screaming children. Racks, cranes, moving stock, staffing, management, and customers demand attention. 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.

1.1 The Problem

Continuous drag-in of contaminants eventually renders the flux solution unsuitable for further galvanizing. The most common flux contaminants are ferrous iron (Fe^{+2} ions) and sulfate SO_4^{-2} (from sulfuric acid pickling). These contaminants are often found to be responsible for increased skimmings and dross, thicker zinc coatings, black/bare spots on parts, and other cosmetic degradation. Frequent disposal of contaminated flux is prohibitively expensive. The flux may be batch-treated to remove some contaminants, but this process takes several days, requires large chemical readjustment, and creates large volumes of sludge for disposal.

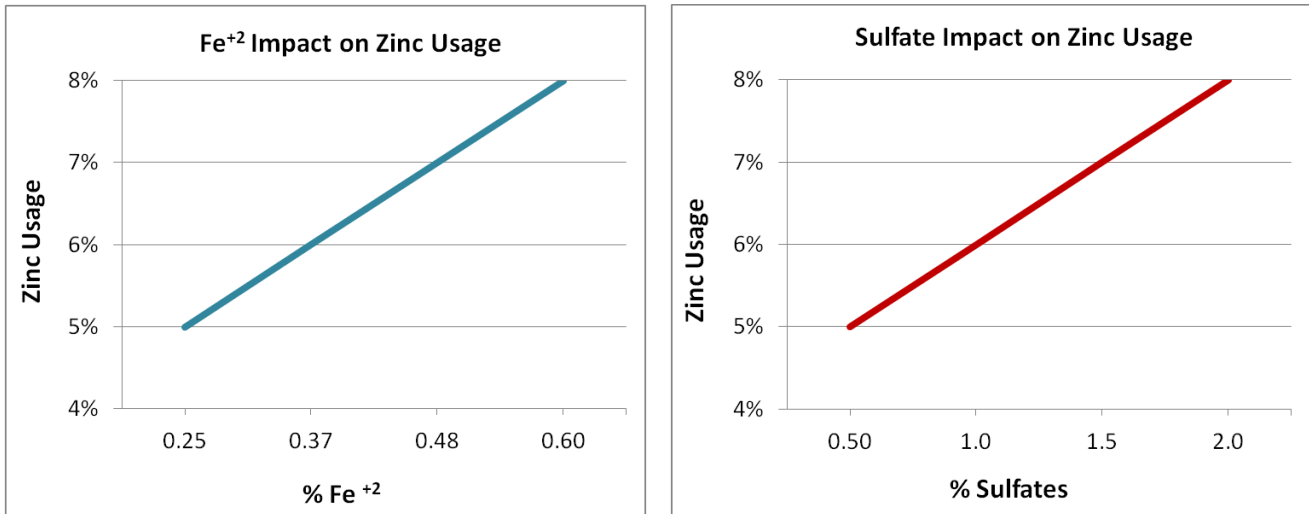
Rather than disposing of the contaminated flux solution, another approach is to continuously remove the contaminants. The fundamental challenge with this approach is removing dissolved contaminants such as ferrous and sulfate ions while retaining the essential zinc ammonium chloride which is in the flux. Another concern is the introduction of foreign chemicals to the flux solution. Any approach to contaminant removal from the flux tank must leave the solution in better condition.

1.2 Effect of Iron and Sulfates on Gross Zinc Usage

To quantify the negative effects of a contaminated flux tank, flux data was collected from selected galvanizers over several years. The increase in sulfate and Fe^{+2} (ferrous) from a fresh tank until it was dumped with nearly 2% sulfate and 0.6% Fe was tracked against the percentage of Gross Zinc Usage (GZU) and skimmings.

It should be noted that the galvanizers operated with a variety of flux Ammonium Chloride Number (ACN) analyses over the data collection, so the following curves represent general trends rather than hard numbers. The combination of the two contaminants contributes to the high GZU.

Figure 1- Contaminants in Flux Tanks



1.3 Cost per Million Pounds Galvanized

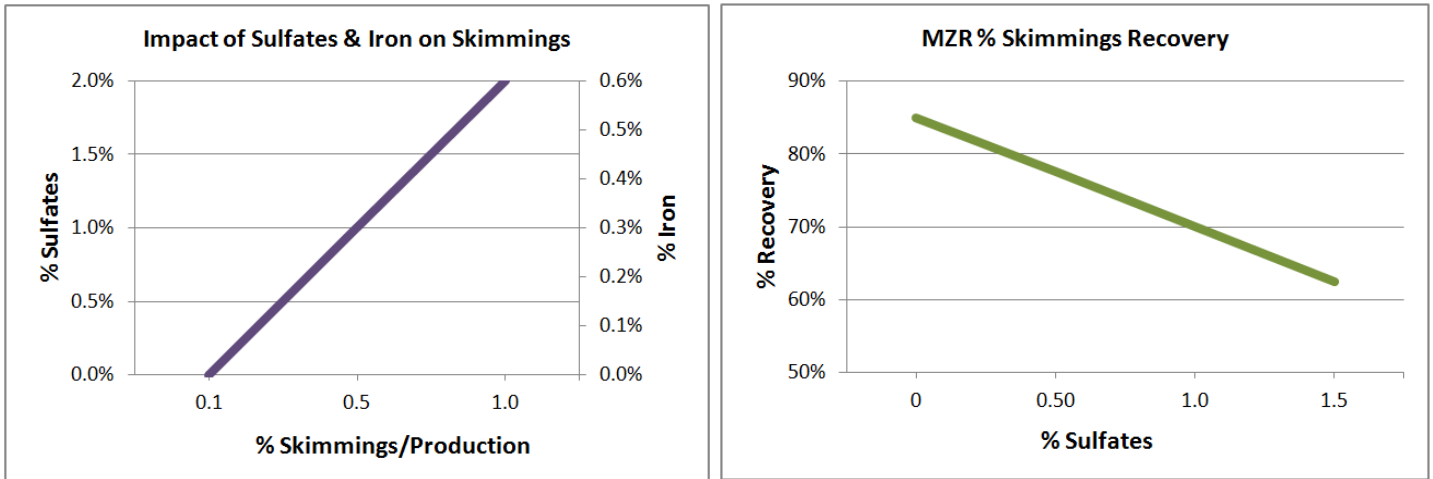
Probably the most followed variable in any galvanizing operation is the Gross Zinc Usage (GZU). It is simply the weight of zinc consumed in the galvanizing process compared with the weight of steel galvanized. Although different alloys, thicknesses, surfaces, fixtures, and shapes may account for some differences in GZU, we have focused our data on two captive galvanizers who coat the same products, with an annual production between 50 and 75 million pounds per year. By following their data through a fresh flux tank to the disposal of the tank, we were able to generate trends that can be applied to other galvanizing operations.

In both of the captive galvanizing plants, percent GZU was approximately 5% at the beginning of the “fresh flux” cycle. One operation let the contaminants build up and their ACN drop. The impact was a GZU in excess of 8%. The second galvanizer adjusted the ACN midstream, but the GZU also rose to over 6.3%. The net effect on both galvanizers was a loss of GZU value between \$450,000 and over \$1.6 million dollars. Variables such as fixtures, pickling practice, and skimming techniques were kept consistent. Both galvanizers used Metallic Zinc Recovery (MZR). Skimmings and dross increased relative to flux contamination.

Ultimately, it is in the best interest of the galvanizer to maintain a clean and chemically balanced flux tank. The table here shows the current LME price to illustrate the effect of a dirty flux on financial losses per million pounds of steel galvanized.

Assumptions	
Cost:	LME Zinc \$1.42/lb + \$0.05 delivery = \$1.47/lb
Coating:	4% by weight
Losses:	1% by weight (fixtures + skimmings)
Consumption:	5% gross zinc usage
Calculations	
Zinc wasted:	1% excess Zn (GZU)
Loss:	\$ 14,700 per million pounds of galvanizing

Figure 2- Impact of Increasing Flux Contamination to Skimming



(Data courtesy of Dr. Tom Cook article on finishing.com Sept. 30.)

1.4 Flux Treatment: Current Practice

Disposal — Currently, many contaminated flux tanks are hauled away and disposed of by an environmental service. The waste volume can define the company as a large quantity generator of hazardous waste. Not only are the disposal costs extreme, but production loss and chemical reloading of the flux tank is very expensive.

Filtering — Often companies filter the flux to remove gross contamination. In conventional (dead-end) filtration the feed is passed through a membrane, solids are trapped by the filter, and the clean filtrate is released at the other end. The filter cake builds up and blinds the filter, requiring replacement. The best filter press might only remove suspended solids between 20 and 200 micron in size and create filter cake that is between 35 and 45% solids. Most sludge sent through a filter press requires a polymer to thicken the suspended solids. Filtering alone will not remove ferrous or sulfate contaminants!

Figure 3 - Dead end filters: cartridge/bag filters, filter press, water filters



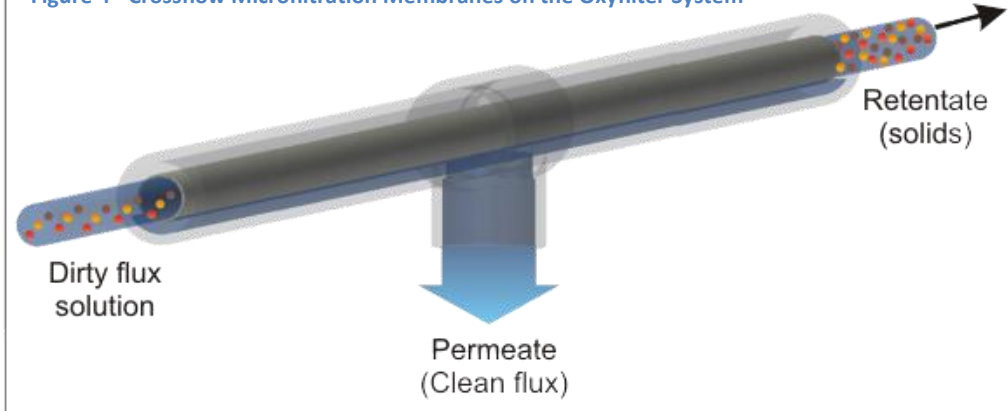
Treatment and Disposal — Another common method of dealing with contaminated flux is “in-tank treatment.” First the pH of the flux is raised to about a pH of 5. Then hundreds of pounds of barium chloride dihydrate salt is added to the now-offline agitated tank to convert the soluble sulfate to insoluble barium sulfate. Barrel quantities of hydrogen peroxide are then added to the flux tank to oxidize the ferrous ion to ferric. The following day, the flux slurry is pumped to a holding tank and the settled sludge removed from the tank. This method is tedious and sloppy. The problems of solution clarification, solids thickening/separation, and shipping hazardous material remain.

1.5 Flux Treatment: Recovery Using Crossflow Microfiltration

None of the current methods provide an optimal solution. Using **crossflow microfiltration**, however, the OxyFilter System provides a cleaner alternative with no added water. The OxyFilter converts iron and sulfate ions to solids in the first stage. The high solids flux is pumped at high velocity through the inner surface of porous tubular membranes, scouring the surface to discourage deposition of the solids. Permeate (clean flux) migrates through the walls of the membranes and is returned to the Flux Tank.



Figure 4 - Crossflow Microfiltration Membranes on the Oxyfilter System



Both “dead end” and microfiltration processes remove suspended solids. The nominal effective solids removal range of any “dead end” filter is between 20 micron and 200 micron. The higher performance tubular membrane microfilter on the OxyFilter System rejects solids less than one micron.

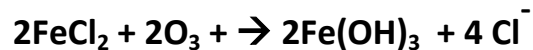
However, both filtration methods initially require chemical treatment to convert the Ferrous and Sulfate contaminants into filterable solids.

Figure 5 - Flux solution before/after the Oxyfilter



2.0 Creating Filterable Solids: the Chemistry

Converting soluble Iron into filterable solids with Ozone Oxidation — The process of removing Ferrous impurities from a flux solution requires the conversion of soluble Ferrous (Fe^{+2}) ions to insoluble Ferric (Fe^{+3}) Hydroxide.

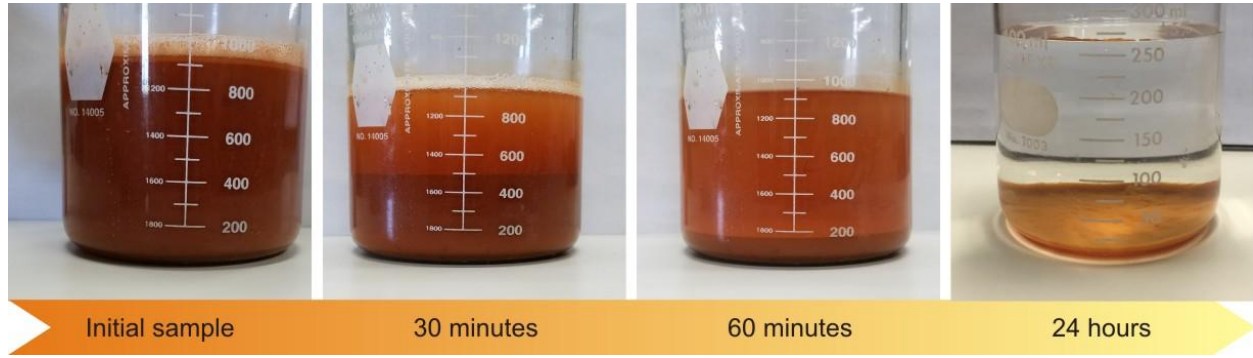


The OxyFilter accomplishes this conversion using Ozone (O_3), a form of oxygen that has one more oxygen atom than the oxygen (O_2) we breathe. This third, loosely-bonded oxygen atom combines with the Fe^{+2} to create Fe^{+3} . Ozone is a highly oxidative gas with similarities to hydrogen peroxide (H_2O_2). Since ozone has a fairly short half-life, any excess ozone from the reaction simply dissipates.

Energy splits oxygen (O_2) into single oxygen atoms (O_1).	Single oxygen atoms form a weak bond with free oxygen molecules to create ozone. $2(\text{O}_1 + \text{O}_2) = 2(\text{O}_3)$	The weak bond is broken. The oxygen attaches to the iron, creating ferric hydroxide. $2\text{Fe}(\text{OH})_3$

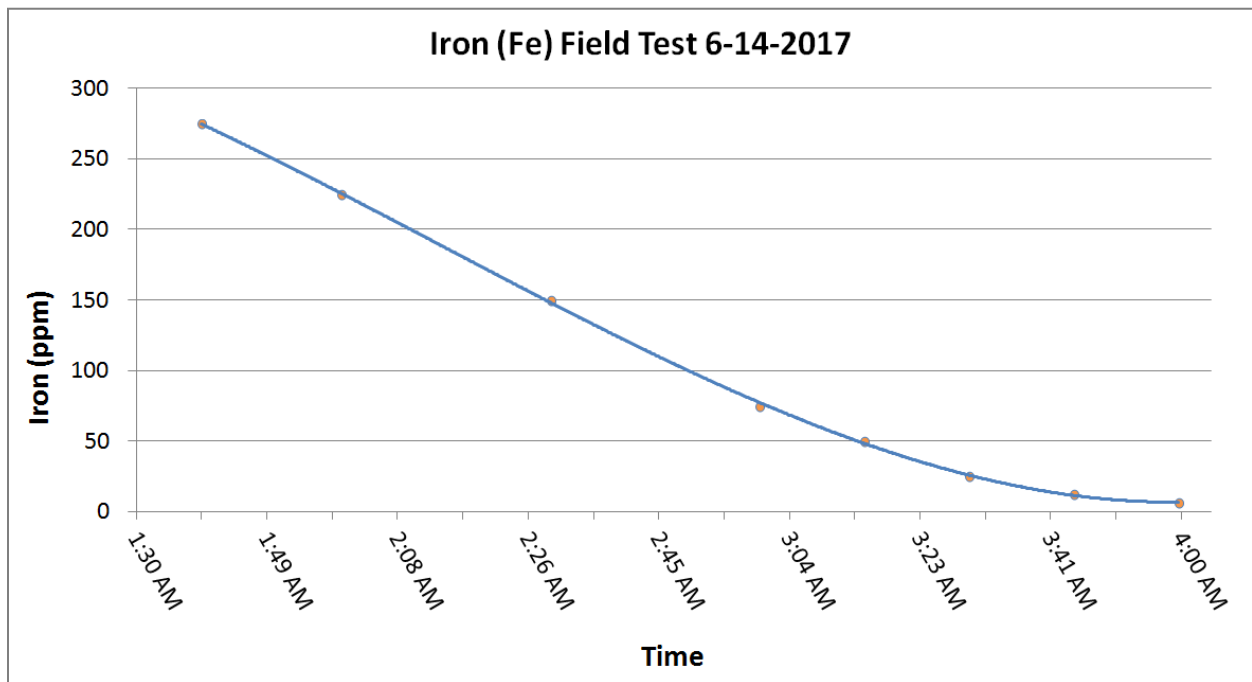
The picture below shows the settling of Ferric hydroxide solids created with the ozone from the OxyFilter System. As shown by the timeline, the solids settle quickly, and after 24 hours the supernatant solution is clear. The supernatant solution is then drained back into the system to become filtered flux solution again. The settled solids are collected, decanted to 5% solids, filtered through paper, and measured to be approximately 45% solids.

Figure 6 - Ferric hydroxide solids settling



Ozone Reaction Efficiency Test — To test the efficiency of using ozone, flux from a working galvanizing process was pumped into the OxyFilter System. A known mass of ozone was reacted with a known mass of ferrous ions during this 150 minute experiment. The graph below 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.

Figure 7 - Effectiveness of Ozone on Ferrous ion conversion to Ferric hydroxide solids



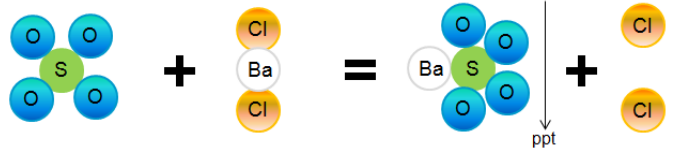
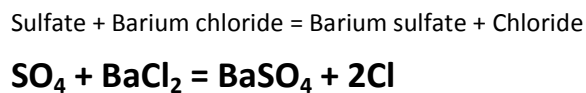
Comparing the Effectiveness of Ozone vs. Oxygen — Since the ozone oxidized the ferrous ions at such an efficient rate, we decided to compare the oxidative capacity of Ozone to 95% Oxygen. We performed the same test with the Ozone generator turned off but the oxygen concentrator still functioning. The flux pH was 4 and the oxygen feed rate was identical to the ozone experiment. The result showed an almost immeasurable oxidation of Fe⁺² (ferrous) to Fe⁺³ (ferric) within the same time period.

Although the visible, orange-colored suspended solids in a standard flux tank prove that a ferrous oxidation is happening in the flux tank, sparging oxygen into the flux tank will not have the desired effect. A strong oxidizer is mandatory to effectively convert the dissolved ferrous ions to ferric suspended solids for removal.

Additional Reasons to Use Ozone — Ozone is one of the most oxidative chemicals commercially available. It is the only 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. Hydrogen peroxide is an alternative oxidizer to ozone, but storage and metering of the chemical can create problems. Hydrogen peroxide reacts violently with organics, chromates, and nitrogen salts and can combust in rare cases.

With both ozone and hydrogen peroxide, there are no unwanted residual chemicals left in the flux solution. The reaction products of both are oxygen. However, technical grade hydrogen peroxide is 35% by weight; therefore, the undesirable consequence is that the 65% water in the peroxide dilutes the flux chemistry. Ozone does not dilute the flux bath during treatment.

Sulfate Removal (for Sulfuric Acid users) — The process of removing Sulfate impurities from a flux solution requires the conversion of soluble Sulfate ions into insoluble Barium Sulfate solids. The most common method is to add Barium Chloride Dihydrate to create the insoluble barium sulfate precipitate.

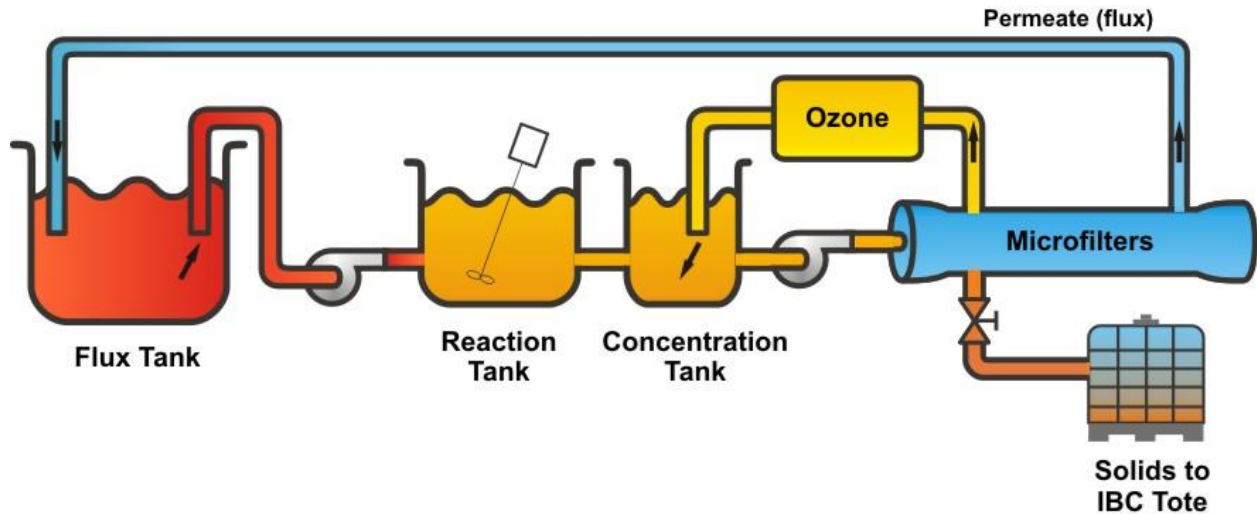


1. Barium chloride is added to microfiltered flux.
2. Solution is agitated as the salt quickly reacts.
3. Filterable barium sulfate solids collect at bottom.



3.0 How Does It Work? The Oxyfiltration Process

Figure 8 - OxyFilter System Using Microfiltration Membranes



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. “ACN” should also be adjusted as needed.

Step 2. Reaction Tank – Dirty flux is pumped to the Reaction Tank. If sulfuric acid is used for pickling, Sulfate ions will be converted into insoluble Barium Sulfate solids by adding a measured amount of Barium Chloride. These solids are created so the Microfilters can remove the resulting Barium Sulfate suspended solids from the flux solution in Step 4. Hydrochloric acid picklers do not need this step.

Step 3. Concentration Tank – In the Concentration Tank, soluble Ferrous (Fe+2) ions are converted to insoluble Ferric (Fe+3) Hydroxide solids using ozone gas. Beta developed a patent pending process to utilize over 95% of the ozone available to the system.

Step 4. Microfilters – After pre-treatment, the flux is pumped at a high velocity tangentially across the surface of tubular, microporous, PVDF membranes. The suspended solids travel quickly through the membranes and return to the Concentration Tank. The solids-free flux solution permeates the membranes and returns to the Flux Tank. This is referred to as *crossflow filtration*.

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 5. 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.

4.0 Case Study

A pilot OxyFilter was installed on the flux tank of a general galvanizer for three months. 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 was the basis of the table below. The galvanizer's rate of iron carryover is based upon two rinse tanks and good rinse practices.

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		
Estimated 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

4.1 Results and Data

Figure 9 - Data from the first full run of the system. (Pump set to 35 Hz.)

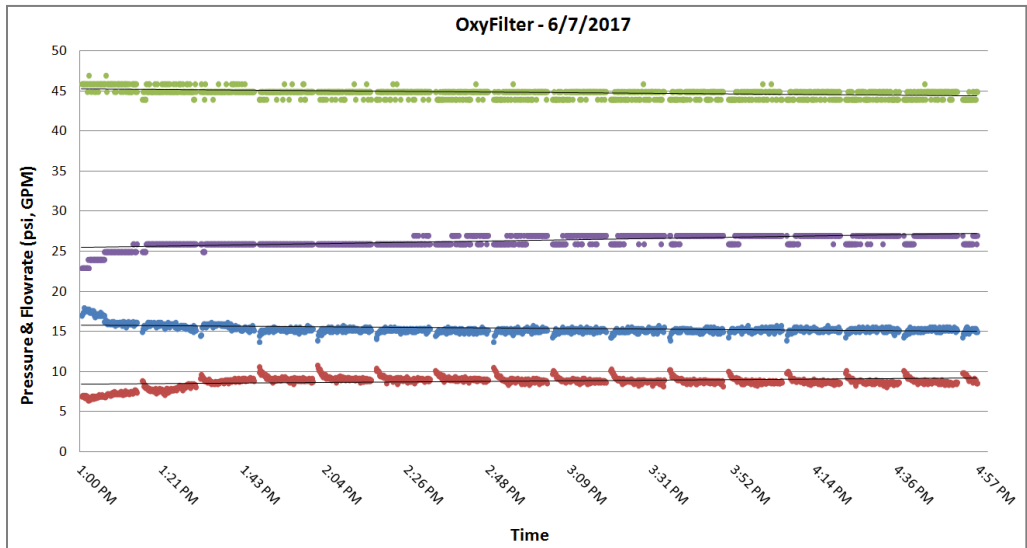
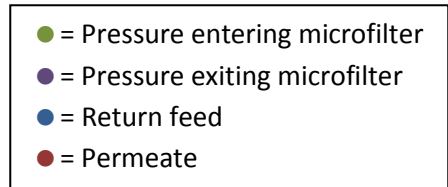
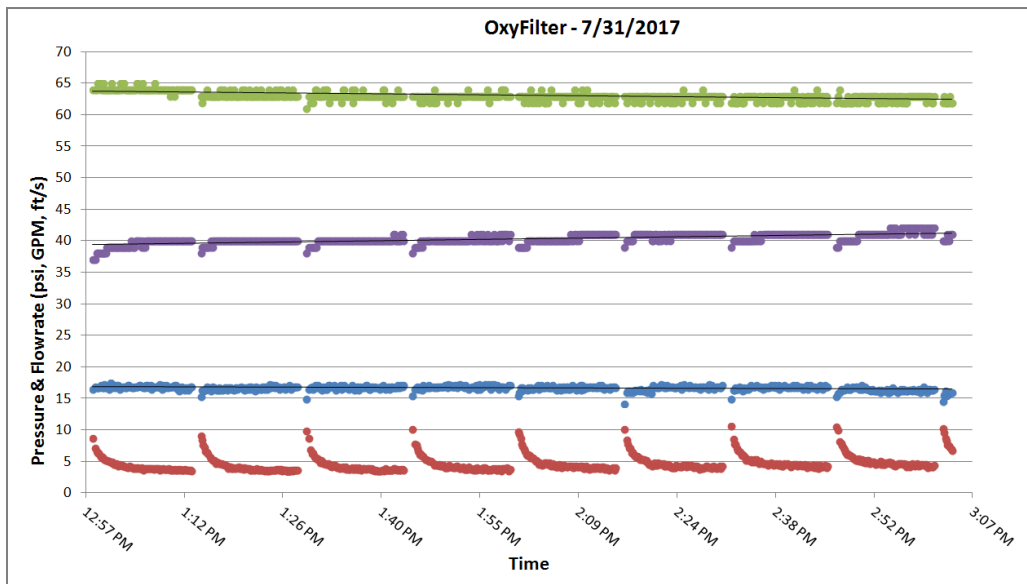


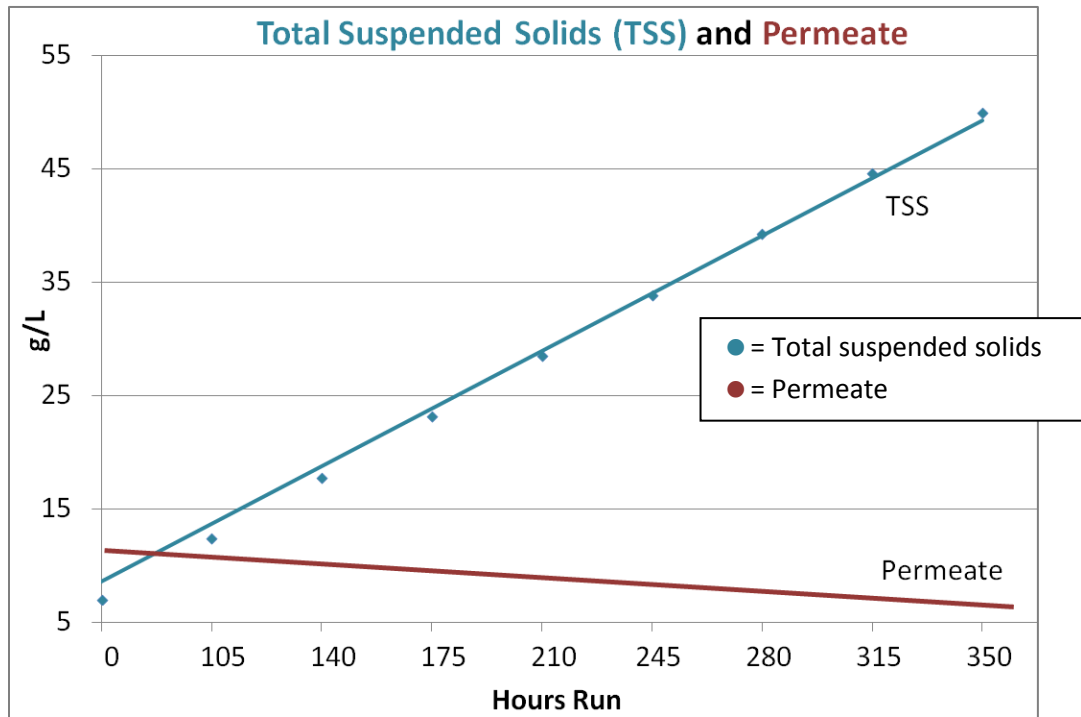
Figure 10 - Data from the OxyFilter System, 2 months and nearly 43 hours of run time after the first run. (Pump set to 50+ Hz)



The pump feed rate was maintained between 8 and 15 feet per second (shown in green) across the membrane surface. This practice allows the high velocity solution to scrub the membrane surface rather than allow solids deposition on the membranes (referred to as *crossflow filtration*).

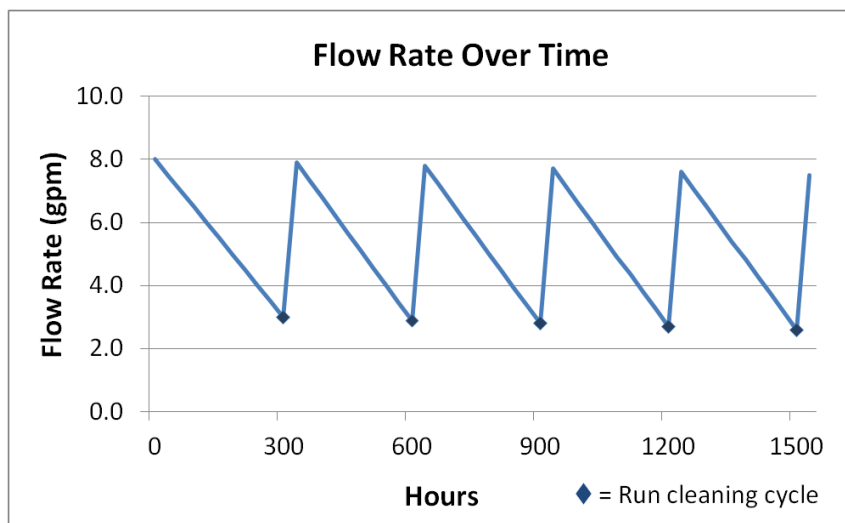
The graphs on the next page show that in the early hours of run time, the permeation rate through the membranes was well above expectations. The “flux” rate (gallons per square foot of membrane surface area per day) was three times projected. The “flux” rate slowed over the 300 to 350 hour cycle to the projected flux rate. After cleaning with five gallons of 5% HCl, the original high flux rate was restored.

Figure 11 - Total Suspended Solids and Permeate passing through membrane. Velocity = 12 ft/sec.



Over the 300 to 350 hour cycle between start up and membrane cleaning, the ferric hydroxide solids accumulate in the Concentration Tank. The solids are drained into an IBC tote at the end of the cycle. The membranes are flushed and soaked for four hours in five gallons of 5% HCl solution.

Figure 12 - Effect of Cleaning Cycle on Flow Rate



The graph above shows the flow rate after cleaning. The system is restarted and the flux rate is renewed to initial performance. This practice of solids draining and decanting followed by membrane cleaning is performed periodically.

4.2 Discussion of Results

Every galvanizer knows that contaminated flux creates problems in production. We discussed the financial impact, but there are several other production and environmental impacts that follow.

This case study involved installation of a full scale OxyFilter System into a general galvanizing plant. An ozone generator sized slightly larger than required was used to oxidize the projected hourly carryover of ferrous ions into the flux tank. The system was originally sized to “turn over” the flux tank in 72 hours. Serendipitously, the microfiltration membranes performed well enough to process the full capacity of the tank in 30 hours.

The process was programmed to start with the push of one button. A PLC was used to run the system automatically and unmanned. Data was collected on a memory card inserted into the PLC. The ongoing data was also available on the HMI screen on the control panel. Some of the charts are included in this paper. The PLC has been retrofitted with a cellular connection and webcam that allows remote monitoring and control by a linked user. This feature also enables remote customer support from anywhere within cellular range.

Once the system was activated, a pump fed flux solution directly from the production tank to the OxyFilter's Concentration Tank. The flux solution reacted with ozone generated from ambient air and injected into the circulating solution. The oxidation process created filterable solids that circulated from the Concentration Tank, through the center of the tubular microfilter membranes, and back into the Concentration Tank. On each pass, the amount of suspended solids in the Concentration Tank increased.

For the first 24 hours, the system's membranes maintained a “flux” rate of 8 to 10 gallons per minute (Figure 9). We worked closely with a membrane fabricator to design a membrane that would allow both zinc and ammonium chloride to pass through the PVDF material while rejecting solids over one micron. The material chosen allowed a full spectrum of pH ranging from high acid to high caustic values. We also had the fabricator build the membrane to withstand temperatures up to 190°F. We expected the “flux” rate to be about 300 GFD (gallons/square foot/day). We were happily surprised to generate over 1000 GFD, which closely matched our average permeate flow rate of 8 gallons per minute.

Every 15 -20 minutes the system automatically shut off the circulation pump, closed the permeate discharge valve, and used a low pressure charge of compressed air to force the ultraclean flux solution in the reverse direction through the membranes. This 15 second “**backflush**” propelled any solids building up on the membrane surface back into the center of the tube. Once completed, the circulation pump ramped back into service to clean the flux. Every 150 hours, the membranes required chemical cleaning.

We modified the PLC program several times, increasing the RPM of the pump motor, varying the system pressure, and tracking a variety of field sensors as the study evolved. By the end of the first phase of the study, we concluded that the system now needs a much longer and more demanding challenge.

5.0 Cost Analysis

Material Costs —The microfiltration membranes on the OxyFilter carry a 36-month warranty and have an approximate life span of three years. Other replacement materials include: pump seals and diaphragm pump seats/balls.

Labor Costs — Daily operation entails turning the system on/off, draining TSS from the Concentration Tank, testing pH, and adding barium chloride. These tasks take 20 minutes.

Every week — Shut down the system for 4 hours while 5 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 min, Inactive time = 4 hrs

Utilities —Electricity consumption is similar to running a household dryer.

6.0 Summary

Most customers will realize a payback in < 6 months. Production benefits include a decrease in:

- Gross zinc consumption
- Skimming
- Product re-runs

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.



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