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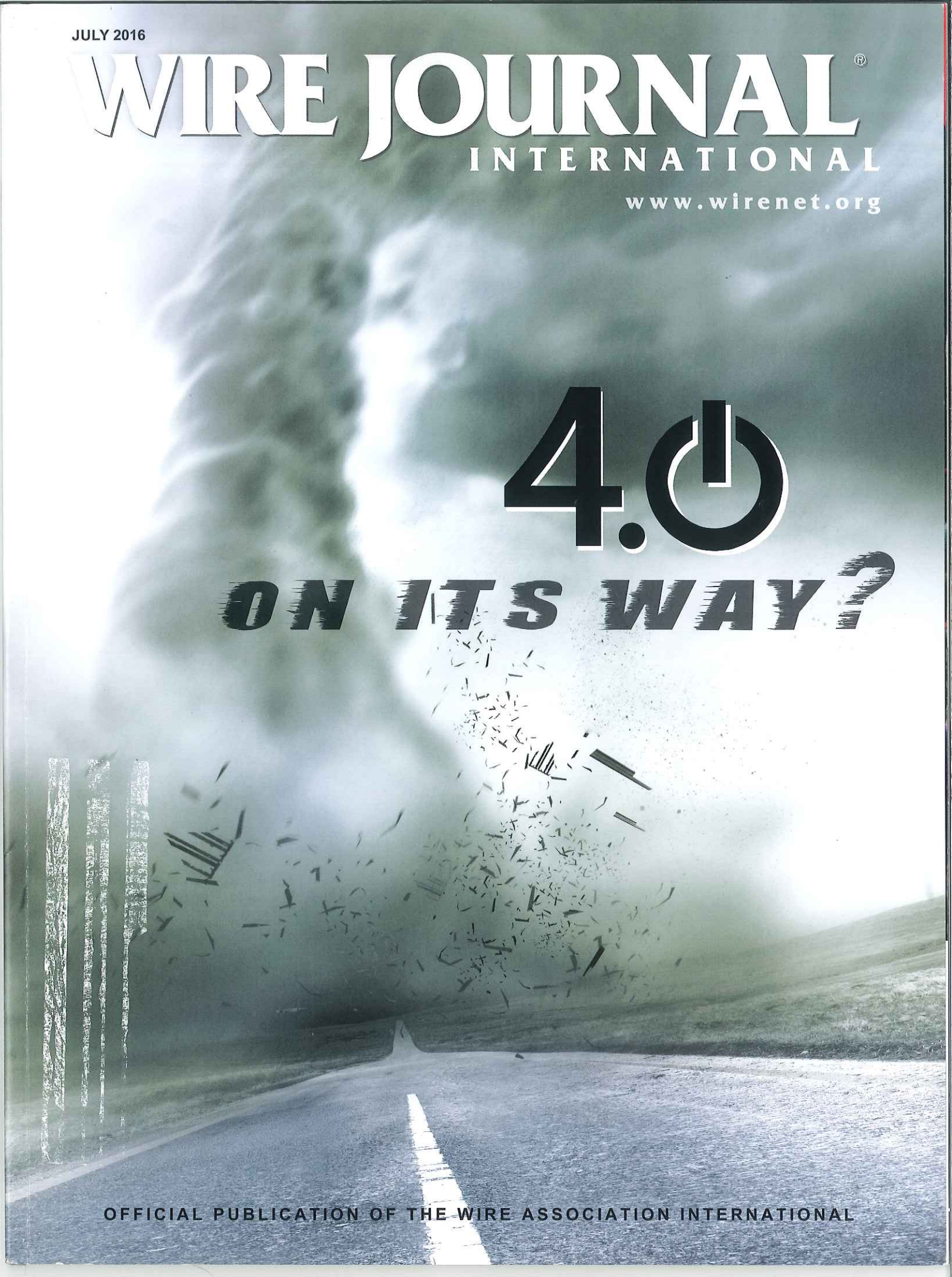

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Acid purification: technical and economic benefits for the wire industry

This case study of a company's experience in trying to improve its use of chemicals found that an acid purification process—which is not the same as acid regeneration—when deployed with an appropriate filtration system, can be beneficial for both improving employee safety as well as reducing expenses.

By Dr. Roger Francois and C. Tom Philipp, P.E.

This paper presents a case study of one of its customer's experiences deploying its technology, in tandem with its efforts to install a filtration system. Each element is integral to achieving the desired results.

Much of the focus in this paper is on the choice of filtering systems, but a key to the process includes the use of catalyzed silicate chemistry that was developed some 25 years ago by the late Dr. John Wagner. It was first used commercially in 1999 in an electroplating shop. In 2003, PRO-pHx, Inc., was formed to expand the applications of the chemistry into the wire, HDG, steel fabricating, electroplating and electro-polishing industries.

The catalyst is held in solution with water-soluble sodium silicate. The catalyst changes the solubility of ferrous chloride and ferrous sulfate into insoluble iron precipitates. Organics normally present in acid tanks are also precipitated. Other common di and trivalent metals like zinc, nickel and aluminum are also precipitated. The process converts contaminants (metals and organics) into insoluble precipitates that are removed by continuous filtration. This process is acid purification technology, not acid regeneration technology, and when properly used with an effective filtering system it can eliminate the need for acid dumps. Below is experience of one multinational wire company.

Wire project

During 2007, a company's corporate environmental department in Europe did an initial evaluation of the process feasibility. One of their U.S. wire plants was selected for a full plant trial. This plant produces approximately 35,000 tons/yr of zinc-coated and electro-galvanized wire from one line. The plant has two 800-gallon hydrochloric acid (HCl) pickle tanks that typically operate at 160°F. The last pickle tank is followed by a vacuum recovery system and a 12-stage counter current rinse system.

The customer evaluated four filters: a 2008 Global 1x PVC, a 2009 Westech Gravity bag filter, a 2011 Siebec bag and cartridge and a 2012 Global 2x CPVC. In 2008, a Global 1X (one chamber) PVC fully automatic back-pulsing filter system was installed. This 1X system, which is typically rated at 5 lb of iron precipitate per backwash cycle, proved to be undersized for the iron dissolving rate. Also, a high concentration of acid vapors plus a chemical leak destroyed the control panel within six months. Data collected during this period indicated that the chemistry performed as represented. Later, it was decided to use a high-capacity, gravity-bag filter manufactured by Westech in Tulsa, Oklahoma. The filter, containing 20 filter bags, did remove the precipitates; however, the operator had to enter an enclosure to remove/replace the bags. This was a safety problem due to the hot acid vapors, and its use was discontinued.

The next filter system evaluated was supplied by Siebec. Two Model P-52 filters were purchased. One a P-52 unit (two chambers) was equipped with a total of eight bags. The second P-52 unit contained a total of eight L-TECH cleanable and reusable 20-micron cartridge filters. New bags or cartridges would provide two to three days of service before cleaning was required. Subsequent reuse of cleaned bags and cartridges gave service life of one to two days and gradually deteriorated to one day or less.

The cartridges and bags had to be removed from the 160°F acid solution, which posed safety problems. The labor expense required to remove, clean and replace the filter elements made an automatic filter mandatory.

In July 2012, a Global 2X CPVC fully automatic filter containing 10 permanent 20-micron bags was placed into operation. The filter will automatically backwash on either pressure differential or time. Typical backwash frequency has stabilized at approximately 90 minutes. To reduce the hydraulic load to the wastewater treatment system, a combination of rinse water and scrubber blowdown water is collected and used for backwashing. The Global filter has a purge cycle to remove unfiltered acid prior to backwashing. See Fig. 1.

The filter has operated trouble-free for 33 months and the original 20-micron permanent filter bags are still being used. Precipitates are retained on the outside of the

What's noteworthy in this paper

WJI: What are the primary benefits of the acid purification technology?

Philipp: You have to understand that change is not necessarily easy, but if a manufacturer that uses traditional acid pickling considers what they could be doing, the potential bottom-line improvements are pretty amazing. What's possible? With a proper filtration setup and our products, one customer was able to reduce its virgin HCl purchases by 30 to 50%. Using our 80 g /l HCl concentrations in the pickle tank makes it feasible to eliminate pickle tank decants or dumps, and that, in turn, eliminates the need for an alkali neutralizing agent. Further, the lower acid concentrations in the rinse waters reduces by 50-70% the quantity of alkali for neutralization. This is an across-the-board, win-win deal for manufacturers currently using a traditional method.

WJI: Why is the volume of wastewater filter cake reduced with the chemistry?

Philipp: Metals are precipitated directly by the chemistry; therefore, an alkali is not necessary. Without acid purification, alkali is first required to raise the pH of pickle tank dumps and rinse water before alkali is used to form ferrous hydroxide. Ferrous hydroxide with six waters of hydration increases the volume of filter cake compared to the very dense ferrous silicate precipitate.

WJI: What is the effect on wire cleanliness from acid purification chemistry?

Philipp: Wire cleanliness is improved because the g/l of HCl (or H2SO4) and g/l of contaminants (ferrous chloride, organics) are held constant due to the precipitation chemistry and automatic continuous filtration.

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bags prior to backwashing with a combination of air and water. One automatic valve did require replacement. The total cost of the filter system was $42,000, including two pumps and spare parts. It is important to communicate the actual acid concentration and temperature to the filter supplier to allow them to select the right grade of construction materials for the filter unit. See Fig. 2.

Fig. 3 shows the classic formation of ferrous chloride as the acid concentration decreases. As the iron concentration approaches 80 g/l, a portion of the bath must be decanted. No acid was fed during the 500 minute evaluation. Fig. 4 shows the benefits of the chemistry and continuous filtration. In this case, acid was fed continuously and the iron gradually dropped from 74 g//l'to 70 g/l. After several weeks of operation, plant personnel gradually reduced the acid concentrations to 80-100 g/l HCl and the iron now ranges from 40-80 g/l Fe.

Project economics

The consumption of the catalyzed reagent is 0.06 liters/ton of production with acid consumption at 350 Kg 32% HCl/day. Plant data has confirmed the following:

	Before	After
Bath Concentration g/l HCl	160	80
Bath Decants	Yes	No
Iron Concentration g/l	100 Max	40 -80
Virgin HCl Reduction	None	30%
Lime Neutralization Reduction	None	70%
Filter Cake Reduction	None	65%

African wire project

Many of the larger HDG and wire plants send acids to central thermal acid regeneration facilities under long term contracts. At the thermal facility, the metals (primarily iron) are removed and 16% HCl is produced. The recovered acid is shipped back to any customer.

Whereas thermal recovery is a preferred environmental alternative to chemical neutralization and land fill disposal of solids, the drawbacks are: excessive recycle costs – ($0.65/gal); in and out hauling of dilute acids; and storage requirements for hazardous waste acid.

The catalyzed acid purification chemistry was first used in Africa at several electroplating shops. Based on these successful applications, a major wire company began an investigation in 2013. The wire company has two continuous wire lines that produce approximately 50,000 metric tons/yr of galvanized wire.

Based upon the U.S. wire data, the plant installed a Global 2x CPVC filter on one of their lines. The line has two 7,600 liter HCl pickle. Fig. 5 shows the flow schematic for the trial line. One problem immediately developed: the filter cycle was much shorter than required for continuous operation. Several replacements of the permanent membranes were required and the membranes were quickly fouled. This initial problem was corrected. Rinse water was used for backwashing and the volume of rinse water was insufficient for backwashing, so the use of city water solved that problem. Also, calcium soaps were used that form insoluble solids in the pickle tanks. Both pickle tanks were then completely cleaned and the chemistry and filtration resulted in normal operation. See Fig. 8.

The one line has now operated successfully for nine months and plant management has issued a purchase order for the second line.

The Global fully automatic filter is preferred for applications where the use of standard cartridge filters would be uneconomical due to kg/day of iron dissolved. The six filter cycles are described below:

Cycle	Function
Service	Filtered acid to pickle tank
Blowdown	Unfiltered acid to pickle tank
Fill	Cylinder fills with water
Backpulse	Air & water discharge solids
Blowdown	Cylinder emptied of fluid
Fill	Cylinder fills with acid

The total time required to clean a filter cylinder is five to seven minutes. With a duplex unit, one cylinder remains filtering while the second cylinder is in backwash.

With continuous removal of dissolved iron, which is precipitated by the chemistry, periodic decants or dumps of the pickle tanks has been eliminated. This greatly reduces the use of the neutralization chemical and also reduces the volume of filter cake produced per the following:

It is common practice in the wire industry to decant a portion of the pickle bath to control the iron concentration. For a 5,000 liter bath, decanting 1,000 liters per week is normal. The amount of caustic required to precipitate the iron and to neutralize the acid in 1,000 liters of 160 g/liter HCl and 100 g/liter Fe can be calculated from the following equations:

$$FeCl_2 + 2NaOH \rightarrow Fe(OH)_2\downarrow + 2NaCl \quad \textbf{Eq. 1}$$

$$HCl + NaOH \rightarrow NaCl + HOH \quad \textbf{Eq. 2}$$

The amount of caustic required for these two reactions for 1,000 liters is 318 kg of 100% caustic. The sludge produced is 161 kg (dry weight basis), which is actually 322 kg assuming the filer cake is 50% dry solids.

Since the catalyzed reagent eliminates decants, the annual savings in caustic required for neutralization and iron precipitation would be 15,900 kg/yr. of 100% caustic. Annual sludge production is estimated to decrease from 16,100 kg/yr. to approximately 7,000 kg/yr. The reagent eliminates 100% of the caustic used for iron precipitation and acid neutralization (i.e., no decants) and 50% of the caustic used for rinse water neutralization

Economics

Based upon one line producing 30,000 MT/yr, the following economics were proven:

Historic cost for regenerated acid	$116,800
Initial cost: equipment installed	$ 43,950
Annual operating cost: chemistry/utilities	$ 35,830
First year savings	$ 37,020
Future yearly savings	$ 80,970
Average monthly savings for first 5 years	$ 6,015
Period to recover investment	6.5 months

The reduced costs for wastewater treatment are not included in the ROI.

Summary

Three wire plants have installed the precipitation chemistry and filtration for continuous acid purification. The technology accomplishes: lower acid pickling concentrations; elimination of bath decants or dumps; reduced virgin acid purchases; reduced neutralizing chemical purchases; reduced filter cake production; and improved process control.

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