

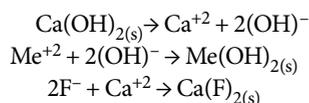
# A crossflow filtration system for heavy-metal wastewater treatment

## OVERVIEW

Semiconductor solder bump operations, in which chips are attached to their substrates using both lead and lead-free plating processes, produce wastewater containing heavy metals (primarily lead and tin) as well as acids, chelates, and oxidizing agents. A projected increase in the loading of this wastewater presented a treatment challenge. A total system solution is presented.

The IBM facility in East Fishkill, NY, manufactures leading-edge semiconductors and semiconductor packaging products. The various processes involved in the production of the final mounted microchips generate a large volume of wastewater. Segregated drains and treatment systems manage the wide range of wastes on site to ensure compliance with governmental discharge regulations.

Wastewater from the solder bump processes was traditionally discharged to a fluoride treatment facility, where it was processed with wastewater from other manufacturing operations using cold-lime softening technology. This treatment consists of fluoride and heavy-metals ( $Me^{+2}$ ) precipitation according to the following predominant reactions:



The resulting solid suspension is separated using high-rate solids-contact clarifiers. The solids volume is further reduced by dewatering using a plate and frame filterpress. This process methodology is inherently robust and has provided a reliable means of treatment for some 20 years. Unfortunately, this precipitation approach for both fluorides and metals suffers because it does not operate in the optimal efficiency range for either reaction. It also suffers from a high sludge-to-wastewater treatment ratio, is susceptible to solids breakthrough in the clarification step, has a large footprint requirement, and is maintenance intensive because of the scaling nature of lime.

An assessment of the fluoride treatment capacity was conducted to evaluate the effects of the increase in lead loading from an expansion of the solder bump operation. It was determined that the expected increase in lead levels could not be removed to acceptable levels using cold-lime softening treatment. The decision was made to construct a new facility that would focus on treatment for removing heavy metals from only the solder-bump operation. The primary design goals were

to develop a treatment methodology that would remove lead (the primary metal constituent) from 100ppm to <100ppb and have versatile scalability to handle a continuous flow range from 50–225gpm.

A paper exercise in process selection narrowed the field to ion exchange and caustic precipitation. Ion exchange was initially bench-tested and produced effluent lead concentrations, which met the discharge requirements. However, lead was very difficult to exchange off the resin and required large regeneration volumes that still required treatment.

Tests of caustic precipitation methods using sodium hydroxide produced favorable results. Bench scale tests on the wastewater established an empirical minimum lead solubility between a pH of 10.0–10.2. Efforts with conventional means to separate and remove these solids met with failure. Many different polymers (anionic, cationic, and non-ionic) were tested with little to no success for flocculation or aggregation of particles. Dead-end filtration with submicron polymeric media worked well for particle separation, but the filters quickly became irreversibly fouled and required frequent replacement in the bench studies. Alternative solid-liquid separation techniques were then evaluated.

Several dynamic membrane technologies were evaluated ranging from microfiltration to reverse osmosis. Each membrane technology offered a wide range of nominal micron ratings, volume-reduction ratios, and versatility. Membrane choices ultimately narrowed to the Microza hollow fiber (HF) crossflow technology by Pall Corp. This crossflow system met the project needs, including those for tight membranes nominally rated at  $0.001\mu m$  (or 13,000 dalton), high-volume reduction, small-space requirement, and modular additions for capacity increase.

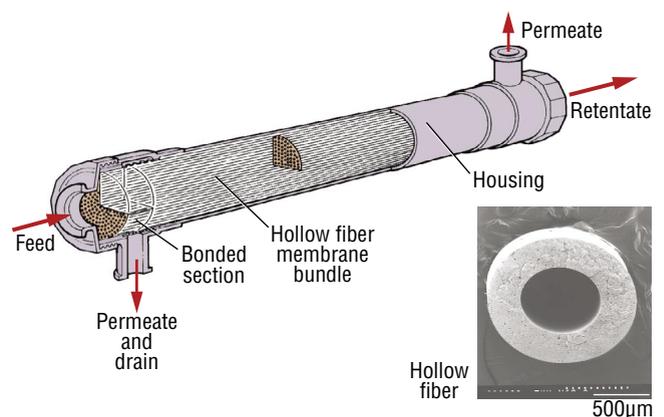


Figure 1. Microza crossflow module.

James MacDougall, IBM, East Fishkill, New York; Vivien Krygier, Pall Corp., East Hills, New York; Eric Sandström, Pall Corp., ret.

## Crossflow technology

The heart of the crossflow system is a hollow fiber solid-liquid separation module that produces a clear (particle-free) permeate and a retentate of high-suspended solids. The modules are operated vertically with the feed entering the lumen of the hollow fiber membranes at a flow rate fast enough to achieve a high velocity, typically 1.5–2m/sec over the membrane surface. This velocity keeps the retained solids in the stream and ensures that the membrane remains clean by maintaining a high shear boundary layer on the membrane surface. The permeate (filtrate) is forced through the permeable walls of the membrane fiber by the system pressure and exits the module as shown in **Fig. 1**. The retentate is recirculated through the module (via external system piping and pumping) until the desired concentration is achieved. Periodically, during the concentration mission, permeate is forced backward through the membrane fiber walls to back flush (reverse filter) the membranes to maintain stable performance.

## Pilot testing

Typically, the composition and characteristics of wastewater vary greatly from day-to-day. Therefore, it is good design practice to perform an onsite pilot evaluation over an extended period of time. To determine the project economics and develop critical design information for the selected HF membrane technology, it is important to establish parameters regarding the flux (the flow rate per unit area of filter) decay over the duration of a filter run, the expected throughput before fouling, and the cleanability (the ability to consistently restore >85% of the original flux after each cleaning).

Similar to a full-scale system, the pilot was operated in a batch mode, in which each batch of wastewater processed represented a concentration mission. The goal of each mission was to feed the system with pH-adjusted wastewater containing precipitated heavy metals, and achieve a target volume reduction of 50–100× that would produce an approximately 1% total suspended solid (TSS) slurry. Pilot runs were conducted over a two-week period to measure the flow rate (flux), the pressure drop across and through the membrane, the total gallons processed in each concentration mission, and, most critically, the removal of lead. At the end of the pilot study, the modules were purposely deadheaded to simulate a worse case condition for membrane surface and depth fouling. To remove the solids and restore the membrane flux, both citric acid (1%) and nitric acid (2%) were tested and found to be effective in fully restoring membrane flux.

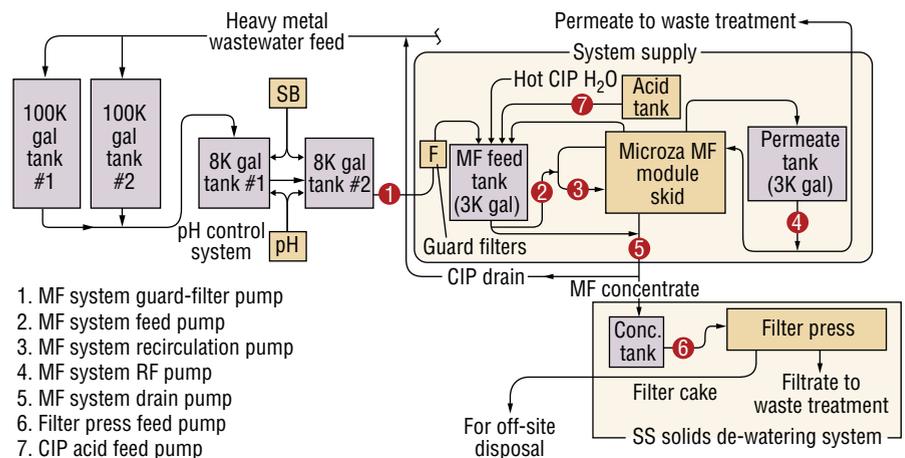
The pilot results demonstrated that the desired performance could be achieved using HF membranes. It would become clear, however, that there were still considerable challenges to design and install a system within the available space.

## Design and installation

The space allocated for the treatment system process equipment was extremely limited. This was especially true for the crossflow filtration system's hydromechanical and control infrastructure, which required about one-third of the space needed for a normal, single-level system

layout. The space limitations were further compounded by the requirement for an expandable system, an N+1 redundancy for critical components, and the need to adhere to IBM's specifications for life-safety, building, and service clearances.

The space limitation issue was solved by using the available overhead space and constructing a mezzanine to contain the hydromechanical and controls infrastructure. Approximately half of the crossflow system infrastructure was installed on this mezzanine. The remainder of this system and the process treatment equipment were installed on the ground floor of the building. The typical arrangement is to have the filtration system modules in parallel. However, a customized series-parallel arrangement enabled a 50% decrease both in recirculation flow pumping requirements and module rack footprint.



**Figure 2.** Process flow diagram of the treatment system.

## Process description

Heavy-metal wastewater from the solder bump operation is collected in two 100,000 gal equalization tanks. Before sending the heavy-metal wastewater to the crossflow filtration system, sodium bisulfite is added to reduce oxidizing agents for membrane protection. This is followed by pH adjustment using sodium hydroxide to precipitate the heavy-metal ions. The metals, now in the form of hydroxide precipitates, are retained and concentrated via the filtration system in a continuously fed batch mode (**Fig. 2**).

Permeate is forwarded to a neutralization treatment system. The concentrated retentate is pumped to a collection tank where it is stored until there is sufficient volume to be processed. The retentate is dewatered in a unique sequence using a standard plate and frame filterpress. First, the filterpress is pre-coated with lime-based sludge from the previously mentioned cold-lime softening process. Then the heavy-metal retentate is applied behind the porous lime pre-coat, producing a sandwich type filtercake. This precoat methodology is important because it prevents issues typically associated with pressing 'sticky' metal hydroxide sludge by itself, such as poor dewaterability, blinding, and cleanup.

Acid cleaning is required when the filtration system capacity significantly decreases, and is performed by recirculating a dilute acid solution. Spent acid wastewater is returned to the head of the system for reprocessing. This acid cleaning protocol is typically referred to as a clean-in-place (CIP). **Figure 3** illustrates a typical operating curve for a 50,000 gal. process mission, in which the HF membranes

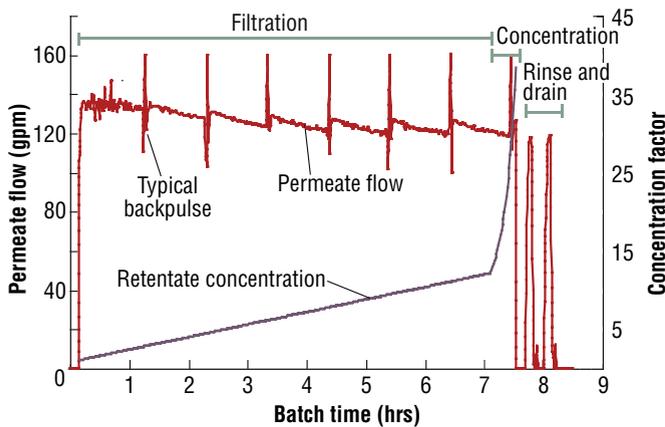


Figure 3. A 50,000 gal. process mission showing symptoms of flux decay before CIP.

have developed symptoms of flux decay because of fouling. Figure 4 demonstrates the flux recovery after a CIP. Note how the same 50,000 gal volume of wastewater can be processed within a shorter duration (7.2 vs. 8.3 hrs), allowing an 11% electrical savings to be realized from less run time on the equipment. CIPs are scheduled every 7 days (or as needed) to maintain high efficiency.

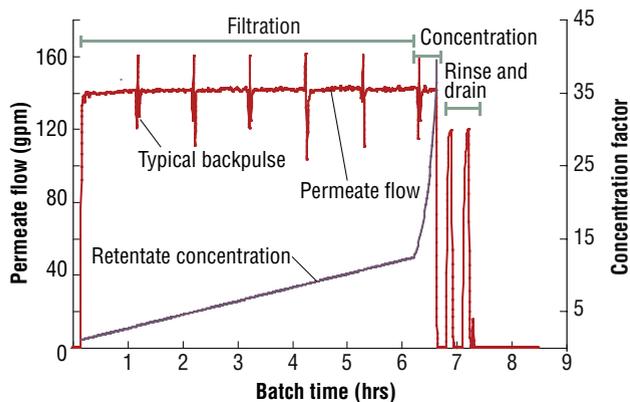


Figure 4. Flux performance after CIP. The wastewater can be processed more quickly.

### Operational challenges

**Membrane deterioration.** The pilot study that was carried out over a period of two weeks appeared to validate the selection of a polyacrylonitrile (PAN) ultrafiltration, HF membrane. Although PAN is susceptible to oxidation by hydrogen peroxide ( $H_2O_2$ ) present in the heavy-metal wastewater, it was thought to be compatible because sodium bisulfite was added upstream to reduce the  $H_2O_2$  to below detectable levels (<1ppm).

However, after six months of operating the full-scale system, membrane fiber breakage occurred. Analysis of the membrane revealed chemical degradation consistent with oxidation, indicating the presence of residual oxidizing agents (Fig. 5).

In order to find a membrane that was compatible with the residual oxidizing agent, a seven-month study was conducted using a specially designed rack that enabled simultaneous evaluation of several membranes. Of the three membrane types evaluated — polysulfone, polyethylene, and PVDF — only the latter did not show any signs of deterioration. There was initial concern regarding the

PVDF membrane since it was available only with a removal rating of 0.1 $\mu$ m. However, it was able to remove lead below the 100ppb threshold, did not foul quickly or irreversibly, was very responsive to acid cleaning, and was tolerant of the high pH environment.

**Membrane fouling.** Citric acid was originally selected to perform a periodic CIP of the modules. However, after six months of operation two problems manifested. First, the frequency of required CIPs increased beyond a reasonable threshold for manually adding the powdered citric acid for each cleaning cycle. Second, citric acid was dramatically reducing flux rates when it was returned to the

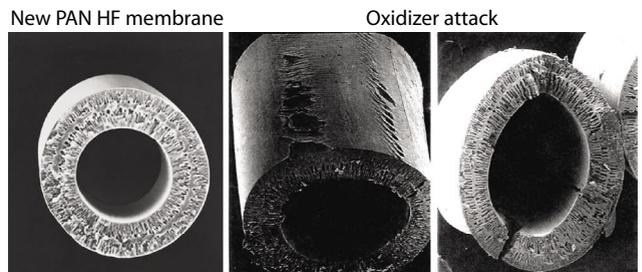


Figure 5. SEM photograph showing physical degradation due to oxidation attack on a PAN structure.

head of the system for reprocessing CIP wastewater. Several alternative acids were tested for the CIP cycle including phosphoric, nitric, and sulfuric. Sulfuric acid showed the most promise with regard to handling, cleaning effectiveness, and the ability to reprocess the resulting acid wastewater. An automated sulfuric acid delivery system was constructed, and the treatment system was reprogrammed to thoroughly clean the membrane modules in situ.

**Chemistry shift.** After ~18 months of trouble-free operation with the new PVDF modules, the flux rates began to radically decrease. Also, high levels of lead were breaking through into the permeate. An autopsy of a module revealed the presence of a white powder plugging the inside and coating the outside of the fibers. The powder was identified by x-ray diffraction as being a combination of lead sulfate and lead sulfite.

Table 1. Comparison of operating metrics

	Cold-lime softening system	Heavy-metal system
Wastewater processed (gpd)	400,000	110,000
Sludge production (lbs/kgal)	22.6	1.1
Operating costs (\$/kgal)		
Chemical	1.37	2.32
Electrical	0.34	0.41
Waste disposal	1.47	0.07
Maintenance (non-labor, \$K/yr)	135	25

A study concluded that the feed and reaction chemistry had changed, and also that the minimum pH solubility for lead had moved downward to 9.0–9.5. Further investigation led to the discovery that lead bisulfite and lead bisulfate were being formed due to addition of the sodium bisulfite reducing agent. These bisulfite reaction products, when precipitated at the lower pH range of 9.0–9.5, were

**Table 2. Characteristics of heavy-metal wastewater before and after treatment**

	Influent	Effluent
pH (SU)	2-3	9.4
Lead (mg/L)	10-200	0.1-0.2
Tin (mg/L)	0.5-2.5	<0.1
Copper (mg/L)	0.2-6.0	<0.1
TSS (mg/L)	1-5	<0.1
Peroxide (mg/L)	100-300	<1

found to constitute a qualitatively important fraction of the overall precipitation step. This fraction supplements the hydroxide precipitation products and enables the system to achieve the low levels of permeate lead needed to make the system work.

### System performance

The operational unit costs for chemical usage, electrical consumption, and waste disposal for the heavy-metal treatment system are slightly higher compared with traditional cold-lime softening (Table 1). However, there are significant savings in maintenance costs and sludge production because of the physical property differences of caustic vs. lime precipitation chemistry. Comparatively, ~15 times more man-hours are required to maintain the cold-lime softening system. The removal efficiencies of the heavy-metal system are summarized in Table 2. Once the chemistry shift issues were identified and corrected, the system has operated in a predictable and reliable manner. All metrics considered,

this system has proved to offer a greater benefit compared with softening technology.

### Conclusion

When the cold-lime softening facility at IBM was no longer able to handle the increased loading of heavy-metal wastewater from its expanding solder bump operation, various techniques were investigated to find an alternative solution. Ultimately, a hybridized system was delivered that combined hydroxide and sulfur-based precipitation with advanced crossflow filtration. The unique reaction chemistry, flexibility of the Microza system, and sludge management make for a system that produces a fraction of the waste at an equitable cost. The heavy-metal treatment system has been in operation since the end of 2000. ■

### Acknowledgment

Microza is a trademark of Asahi Kasei Corp.

**JAMES MACDOUGALL** received his BS in chemical engineering from Clarkson U. and his BS in chemistry from Pace U. and is an environmental engineer at IBM, 2070 Route 52, Hopewell Junction, NY 12533; ph 845/892-1604, e-mail jamesmac@us.ibm.com.

**VIVIEN KRYGIER** received her PhD and BSc in biochemistry from McGill U. and is a senior VP of marketing, microelectronics, at Pall Corp., East Hills, NY; ph 516/801-9155, e-mail vkrygier@pall.com.

**ERIC SANDSTRÖM** received his BS in mechanical engineering from Bradley U. and retired from Pall Corp. in 2004.



2200 Northern Boulevard  
East Hills, New York 11548-1289 USA

1.800.360.7255 toll free (Only in US)  
1.516.484.5400 phone  
1.516.625.3610 fax

Visit us on the Web at [www.pall.com/micro](http://www.pall.com/micro)

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