Heavy Metals Removal/Stabilization with New Microfiltration Technology

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Abstract

The novel Du Pont/Oberlin Microfiltration Technology has recently been demonstrated in EPA's Superfund Innovative Technology Evaluation (SITE) program. Its key features are fine microfiltration at low cost using Du Pont's new Tyvek* T-980 spunbonded olefin filter media coupled with Oberlin's reliable automatic pressure filter (APF).

This new microfiltration technology is best suited for contaminated heavy metal wastewaters and rinsewaters.

However, this new microfiltration technology is limited to low flows, generally less than about 150 gpm. As a consequence, Gore backpulse filters have been used to concentrate the flow by 25-50X prior to Du Pont/Oberlin microfiltration. The Gore backpulse filter assures the ppb metals removal and is much simpler than the conventional Lamella/sand filter combination traditionally used. This paper will describe these two new technologies in detail and will present some typical application results.

** DuPont's trademark for its flashspun HDPE nonwoven filtration medium.

INTRODUCTION

The DuPont/Oberlin Microfiltration Technology was successfully demonstrated by the EPA in their Superfund Innovative Technology Evaluation (SITE) program in 1990 (Refs. 1,2). Excellent 99.95% suspended solids (TSS) and metals removals were demonstrated from the Palmerton, PA Superfund site's contaminated groundwater (Refs. 3,4,5). In addition, filter cake residuals passed both the TCLP and EPTOX leaching tests for heavy metals, with the patented PROFIX* filter aid/stabilization agent used. The excellent filtrate quality achieved was assured by use of DuPont's new Tyvek® T-980** disposable, nonwoven filter medium, which is rated about 1-micron absolute (by standard ACFTD challenge testing methods). Implementation of this technology has been discussed in detail (Refs. 1,2) with many case histories where the technology has been applied. However, many applications require high flows, and since the DuPont/Oberlin Microfiltration Technology is limited to about 3 gpm/ft^2 maximum flux, flows are limited to about 150 gpm maximum/system. Multiple systems can and have been used, but this becomes expensive. Additionally, PROFIX usage becomes high because its use is predicated on maintaining the high flux rather than metals stabilization. As a result, some sort of preconcentration is needed when system flows exceed about 150 gpm. Consequently, this paper addresses this concentration step and how it is combined with the DuPont/Oberlin Microfiltration Technology. Case histories are also presented where this new combined technology has been and will be applied.

Preconcentrating Processes

A number of methods were scouted with a few typical wastes to determine their concentration factors, their propensity to handle variable waste loads, and most importantly, their metals removal. The technologies scouted are listed in Table I along with general advantages/disadvantages and their metals removal ability to achieve ppb effluent levels as well as drinking water standards. Table I shows that:

- A conventional clarifier (or parallel plate type) is proven technology and is quite simple, but metals removal is poor, especially since flocculated metals occasionally overflow and cause high bursts of metal concentrations. Typically, an overflow sand filter is used, but it usually can only remove particles down to about 5-micron and ppb metal levels are difficult to achieve. Thus, this approach was rejected.
- A modification to the clarifier approach is to use metal-adsorbing polymers as developed by the U.S. Bureau of Mines (Ref. 6). Bench testing proved this technology to be feasible, but pilot testing could not be done for economic reasons, particularly since this technology was deemed unproven. As a result, it was also rejected.
- An electrocoagulation process as developed by Electropure (Ref. 7) was also successfully bench-scale demonstrated, but its unproven nature made the plants uncomfortable in further piloting. Hence, it was also rejected despite its low capital and operating costs.
- Abcel™, a proprietary additive for metals removal used in the metal finishing industry, was also proven effective, but its high operating cost, moderate capital cost, and relatively unproven technology precluded its use here.
- Ionsorb™, another proprietary additive from Celite Corp., also was rejected because of its unproven technology and very high operating cost. Subsequent to this program, Celite has withdrawn this product from the market place.
- Memcor, a 0.2µ hollow-fiber PP microfilter developed in Australia (Ref. 8), is well-proven in the potable water and municipal wastewater fields, but its high complexity and high capital cost precluded its use here as well.
- The Gore backpulse filter is a well-proven technology (Refs. 9-12), simple, assures excellent metals removals, and most importantly, is low cost. As a result, it was chosen over the other devices for further evaluation and scaleup.

Thus, this brief comparison of the preconcentrating methods scouted here showed that the Gore backpulse filter was best suited overall for ppb metals removal, simplicity, proven

* enviroGuard's trademark for its patented filter aid/stabilization agent.

technology, and most importantly, low capital and operating costs. It also complemented the DuPont/Oberlin SITE technology very nicely because it concentrates metal hydroxides, for example, 20-50X without any additives at all. As a result, the DuPont/Oberlin SITE technology (Refs. 1,2) can use the Profix stabilization/filter aid agent primarily for stabilization rather than for flux enhancement. Consequently, its dose can be reduced, which in turn lowers cost, but most importantly, reduces waste volume (the major cost item usually in today's environmental climate). Bench testing has demonstrated as much as a four-fold PROFIX reduction by preconcentration, with a two-fold reduction easily achieved. Therefore, preconcentration of metal sludges with the Gore backpulse filter has proven to be quite economical and a viable complementary device to the DuPont/Oberlin Microfiltration Technology, which has been successfully demonstrated in EPA's SITE program and published previously (Refs. 1-5). The case histories presented below will highlight where these combined technologies have been successfully applied.

CASE HISTORIES

Strong-Acid Calcium Chloride Clarification

This application involves a clarifier replacement because the Plant couldn't sell the clarified $CaCl_2$ since too dirty, and underflow sludge had to be hauled off-site at considerable $250M annual expense (Table II). Direct Oberlin filtration was first tried, but although it produced excellent quality $CaCl_2$ (0.3 ppm Total Suspended Solids (TSS) and 0 APHA color), its flux was quite low at 0.43 gpm/ft^2 so multiple systems would be required. As a result, a Gore backpulse filter was successfully piloted (0 APHA color and 4-5% underflow solids), such that the Oberlin system size was reduced almost 20-fold with significant capital cost savings. In addition, the PROFIX dose was reduced two-fold and the cakes still passed TCLP for landfilling (as well as chloride level because the cake was washed in the Oberlin filter). Overall, capital costs were reduced in half and operating costs reduced 50% with this combined Gore/Oberlin system. As a consequence, it was scheduled for implementation until the plant was sold.

Chrome Recovery

This Plant faced extreme EPA regulatory pressure since existing pressure leaf filters couldn't achieve the 2 ppm Cr effluent limit routinely; and the resultant solids were mixed with filter aid so Cr recovery couldn't be done. Direct filtration testing (Table III) demonstrated excellent Cr removals (~0.05 ppm) which were well below the new 1 ppm limit, but fluxes were very low without aids such that capital costs exceeded $1MM. A conventional clarifier with polymer flocculant was next tried but it was very difficult to obtain much less than 5 ppm Cr in the overflow. As a result, the Gore backpulse filter was piloted and a reasonable 0.6 gpm/ft^2 flux was demonstrated with outstanding filtrate quality (0.3 ppm TSS and 0.024 ppm Cr).

Underflow sludge concentration reached almost 6% solids which reduced Oberlin system size almost 50-fold and capital cost about $800M, but of prime importance was that the Cr sludge could be recovered at another $200M annual cost savings. A full-scale system has been installed about a year ago and it has met all expectations to the extent that filtrate quality is typically <0.02 ppm Cr so that the on-line turbidimeter (~0.02 NTU) is used to assure (and validate to the State EPA) the excellent removal in lieu of expensive Cr analyses. Sludge solids are also much higher and typically 12-14%.

Groundwater Metals Removal

This Plant was faced with a VOC groundwater remediation task and piloting showed severe air stripper fouling with solids. Analysis of these solids revealed some heavy metals plus significant iron (Table IV). Cartridge filters were first tried, but they plugged too quickly and a conventional clarifier couldn't achieve the required effluent metals limits. Direct DuPont/Oberlin SITE microfiltration demonstrated excellent metals removal, a very high 2.7 gpm/ft^2 flux, and stabilized cakes (pass TCLP), but projected groundwater flows were quite high so multiple Oberlin systems would be required (at least 3, and most likely 4). As a consequence, a Gore backpulse filter was piloted and excellent metals removals and flux were obtained (Table IV). Sludge solids were also fairly high (6.2%) such that Oberlin size was reduced about 60-fold and PROFIX dose about four-fold (and still cakes passed TCLP). As a result, a complete Gore/Oberlin system was designed for implementation, until the state EPA relaxed the metals limits to the extent that no treatment would be required (i.e., the 8 toxic metals concentrations were fairly low, and Fe, Zn are not regulated).

Mixed Groundwater Metals Removal

This Plant already had two DuPont/Oberlin systems operating quite successfully (Ref. 2), but expanded groundwater treatment required at least one (maybe two) more systems at about \$1.8MM capital. As a consequence, a Gore filter was piloted to determine if preconcentration can reduce hydraulic load to the Oberlin filters and preclude installation of additional systems. Table V summarizes these tests and shows that the Gore backpulse filter achieved excellent filtrate quality (<0.2 ppm TSS and <10 ppb Cu, Zn removals) at a reasonable ~1 gpm/ft^2 flux with Gore's new 0.2μ JGI media. In addition, Gore underflow solids were about 3% (a very high 100X concentration factor from the ~300 ppm TSS groundwater). As a result, hydraulic load could be reduced substantially and the two existing Oberlin systems would have adequate capacity. An added benefit was that the PROFIX dose could be reduced almost four-fold with the more concentrated groundwater. A project is currently being prepared to install a full-scale Gore backpulse filter at significantly less capital (about \$350M).

Metal Cleaning Metals Removal

This Plant uses 10% sulfuric acid to degrease and clean metal parts, and the resultant wastestream required metals removal to meet NPDES discharge limits. Initial clarifier testing (after caustic neutralization) with various polymers could only achieve ~1 ppm metals removal (and only 500 ppb Pb which exceeded the 50 ppb discharge limit). Direct Oberlin filtration produced excellent filtrate quality (<5 ppb Pb and 0.1 ppm TSS) but flux was low (0.6 gpm/ft^2) such that two large systems would be required. On the other hand, Gore backpulse pilot testing demonstrated similar excellent metals removal, a reasonable 0.25 gpm/ft^2 flux, and a reasonable 20X concentration factor to about 1.6% solids. As a result, Oberlin size was reduced about eight-fold and PROFIX dose four-fold (and the resultant cakes still passed TCLP for Pb). A project is now being considered to treat this wastewater in lieu of central wastewater treatment.

Brine System Clarification

This Plant uses a 20% brine for cooling various process equipment. Unfortunately, metals build up in this system as corrosion products and require removal for efficient operation. Analysis revealed that all eight toxic metals were present, including Fe, Cu, Ni, and Zn. Direct clarification was first tried with limited success (Table VII) so a rental-trailer filter press was used with 3:1 PROFIX addition to reduce system solids from about 3000 to 300 ppm. The resultant press cakes passed TCLP for the eight toxic metals. Once the brine system was cleaned, a permanent filter was required to keep it clean. A traditional sand filter was first tried but the particles were much too fine for efficient capture and polymer flocculation was risky in this closed system. A Gore backpulse filter was next tried and outstanding results were obtained (Table VII) with filtrate quality typically <1 NTU turbidity and about 0.2 ppm TSS. The resultant 7-8% Gore sludge was then dewatered with PROFIX in an Oberlin unit with 1/6 the PROFIX dose compared to direct filtration. As a result of these positive results, a project is being prepared to install a Gore backpulse filter system.

SUMMARY

The DuPont/Oberlin Microfiltration SITE technology has been successfully demonstrated to remove heavy metals to ppb levels from wastewaters and groundwaters and simultaneously produce stabilized cakes that pass TCLP with the PROFIX filter aid/stabilization agent. Practically, however, it's limited to about 150-250 gpm flows, above which wastewater concentration becomes more economical. The work here has demonstrated a suitable concentrating device, the Gore Backpulse filter, which complements the DuPont/Oberlin SITE technology very well. Extensive piloting and one installation have demonstrated excellent ppb metals removals at reasonable fluxes, significant capital cost savings, lower PROFIX demand, and significant 20-100X concentration factors depending on waste characteristics. In addition, the Gore filter operates without filter aid and/or polymer flocculant addition. Consequently, the environmental engineer/contractor now has a complete separation system to guarantee ppb metals removals and stabilized cakes for non-hazardous landfilling at high flows.

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TABLE I

PRECONCENTRATION DEVICES EVALUATED

	Device	Proven Technology?	Complexity?	Metals Removal	Capital Cost	Operating Cost
1.	Clarifier	Yes	Low	Poor	Moderate	Moderate
2.	Clarifier (w/Bureau of Mines' polymers)	No	Low	V. Good	Moderate	Moderate
3.	Electro-Coagulator	No	V. Low	V. Good	V. Low	Low
4.	Abcel™	No?	V. Simple	Excellent	Moderate	High
5.	Ionsorb™	No	Moderate	Excellent	Moderate	V. High
6.	Memtec	Yes	High	Excellent	High	Low
7.	Gore Backpulse	Yes	Simple	Excellent	Low	Low

TABLE II

STRONG-ACID CALCIUM CHLORIDE CLARIFICATION

Unit	Filter Aid?	Polymer?	Filtrate TSS (ppm)	APHA Color	Flux (gpm/ft^2)	% Solids	Pass TCLP?
Clarifier	No	Yes	>300	>500	—	1-2	No
Oberlin*	Yes	Yes	0.3	0	0.43	63	Yes
Gore Backpulse	No	No	1-4	0	0.26	4-5	No
-Oberlin**	Yes	No	3.5	0	0.33	40	Yes

* Direct filtration with Oberlin produced low flux.

** Oberlin dewatering of Gore concentrated 4-5% sludge.

TABLE III

CHROME RECOVERY

Unit	Filter Aid?	Polymer?	Filtrate TSS (ppm)	Effluent Cr (ppm)	Flux (gpm/ft^2)	% Solids	Recov-erable?
Pressure Leaf	Yes	Yes	<10	2	1.0	~1	No
Clarifier	No	Yes	<20	<5	—	2-3	Yes
Oberlin*	Yes	Yes	0.4	0.06	0.7	40	No
Verti-Press*	No	Yes	0.3	0.05	0.07	40	Yes
Gore Backpulse	No	No	0.3	0.024	0.6	6	Yes?
-Oberlin**	No	No	1.7	0.19	0.03	32	Yes

* Direct filtration too costly.

** Oberlin dewatering of Gore concentrated ~6% sludge.

TABLE IV

GROUNDWATER METALS REMOVAL

Unit	Filter Aid?	Polymer?	Filtrate TSS (ppm)	Effluent Metals (ppm)		Flux (gpm/ft^2)	% Solids	Pass TCLP?
				Fe	Zn			
Clarifier	No	Yes	24	3	0.8	—	1-2	No
Oberlin*	Yes	Yes	0.1	<0.1	<0.01	2.7	59	Yes
Gore Backpulse	No	No	0.7	<0.1	0.15	2.0	6.2	No
-Oberlin**	Yes	No	1.8	<0.1	0.1	0.25	50	Yes

* Direct filtration too costly.

** Oberlin dewatering of Gore concentrated 6% solids sludge.

TABLE V

MIXED GROUNDWATER METALS REMOVAL

Unit	Filter Aid?	Polymer?	Filtrate TSS (ppm)	Filtrate Metals (ppb) Fe	Cu	Zn	Flux (gpm/ft^2)	% Solids	Pass TCLP?
Oberlin*	Yes	Yes	<0.2	ND	<10	<20	2.0	40	Yes
Gore Backpulse**	No	No	<0.2	ND	<10	<10	1.0	~3	No
-Oberlin	Yes	No	<0.2	ND	20	100	0.5	40	Yes

* Direct filtration implemented.

** Gore Backpulse preconcentration to be done for capacity increase.

TABLE VI

METAL CLEANING METALS REMOVAL

Unit	Filter Aid?	Polymer?	Filtrate TSS (ppm)	Filtrate Metals (ppb) Cu	Zn	Pb	Flux (gpm/ft^2)	% Solids	Pass TCLP?
Clarifier	No	Yes	≤30	≥1000	≥1000	≥500	—	2-4	No
Oberlin*	Yes	Yes	0.1	60	150	<5	0.6	42	Yes
Gore Backpulse	No	No	0.2	300	130	<5	0.25	1.6	No
-Oberlin**	Yes	No	0.5	290	260	9	0.32	46	Yes

* Direct filtration much too costly.

** Oberlin dewatering of Gore concentrated 1.6% sludge.

TABLE VII

BRINE SYSTEM CLARIFICATION

Unit	Filter Aid?	Polymer?	Filtrate TSS (ppm)	Filtrate Metals (ppb) Fe	Cd	Cr	Pb	Zn	Flux (gpm/ft^2)	% Solids	Pass TCLP?
Clarifier	No	Yes	20	44	1	1	10	6	—	~1	No
Filter Press*	Yes	No	24	53	1	1	12	7	0.05	65	Yes
Gore Backpulse	No	No	0.2	5	ND	ND	0.5	1	0.16	7-8	No
-Oberlin**	Yes	No	0.3	1	—	—	—	—	0.32	62	Yes

* Direct filtration implemented but only 90% solids removal.

** Oberlin dewatering of Gore concentrated 7-8% sludge.