Complex Microfiltration Behavior of Metal Hydroxide Slurries - 11376

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Abstract:
Crossflow filtration is to be a key process in the treatment and disposal of approximately 60,000 metric tons of high-level waste stored at the Hanford Site in Richland, Washington. Pacific Northwest National Laboratory is assessing filter performance against waste simulant materials that mimic the chemical and physical properties of Hanford tank waste. Prior simulant studies indicate that waste filtration performance may be limited by pore and cake fouling. To limit the shutdown of waste treatment operations, the pre-treatment facility plans to recover filter flux loses from cake formation and filter fouling by frequently backpulsing the filter elements. The objective of the current research is to develop an understanding of the roles of cake and pore fouling and potential flux recovery through backpulsing of the filters for Hanford waste filtration operations. Metal hydroxide wastes were tested to examine the role of particle-filter interaction on filter performance.

1. Introduction

Approximately 60,000 metric tons of high-level waste (HLW) sludge is contained in 177 underground storage tanks on the Hanford Site in Richland, Washington. This waste was generated during the more than 45 years that plutonium and other nuclear materials were produced at Hanford. Characterization studies have identified more than 150 different significant sludge-bearing streams [1]. This sludge phase is typically a blend of metal hydroxides and oxides. The most common species include aluminum hydroxides (predominately gibbsite and boehmite), iron hydroxides (for example, goethite), uranium oxide, and a broad spectrum of other oxides and hydroxides [2]. Average (volume %) particle-size distributions (PSDs) of these solid particulates range from less than 1 micron to greater than 10 microns [3].

As part of a U.S. Department of Energy (DOE) agreement with the U.S. Environmental Protection Agency and the state of Washington, the HLW sludge is destined to be removed from underground storage and vitrified at the Hanford Tank Waste Treatment and Immobilization Plant (WTP). Before these HLW waste slurries are vitrified, they will be processed at the Pretreatment Facility (PTF) to remove glass-limiting elements such as aluminum and phosphorus from the HLW to improve the solubility of the radioactive waste into the glass matrix. The first step in treating HLW sludge at the PTF will involve crossflow ultrafiltration to dewater the sludge phase (for an example of the crossflow filter used in this work, see **Figure 1**). The planned ultrafiltration process involves concentrating the feed streams from 4 wt% to 17 to 20 wt% using porous stainless steel filter elements. The full-scale filtration unit will consist of five filter bundles with each bundle consisting of 241 parallel flow ½-inch (ID) tubes up to 120 inches in length.

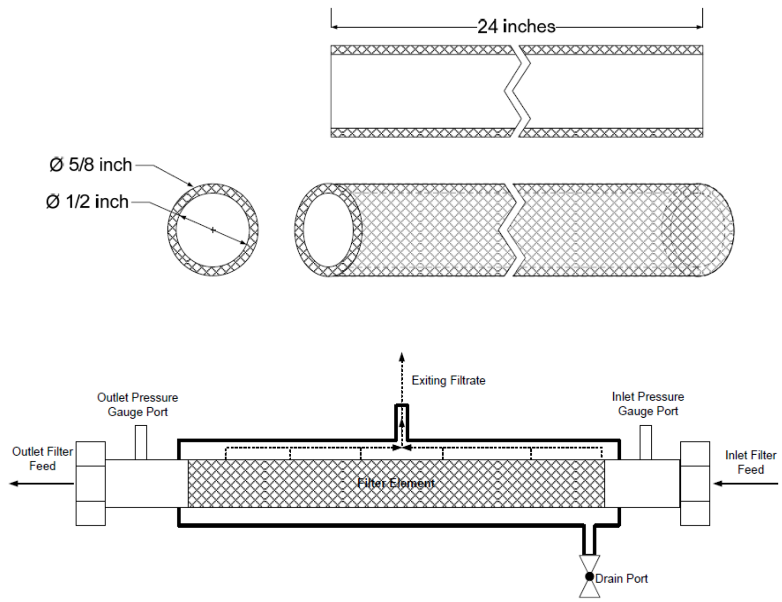

Figure 1. Crossflow filtration unit used in this work.

While most industrial ultrafiltration processes are characterized by relatively constant feed streams, the waste stream that will feed the PTF is highly variable in both chemical speciation and physical properties. Because of the high cost of working with highly radioactive materials, only a limited number of actual waste filtration trials have been conducted to confirm ultrafiltration performance with HLW. Previous test samples were selected based on the initial tank processing sequence and do not fully cover the broad range of feeds expected to be processed over the lifetime of the plant. Consequently, it is desirable to develop methods to estimate filtration performance for the balance of the Hanford HLW based on available characterization data.

To further that end, a series of actual waste filtration/leaching tests were recently performed at the Pacific Northwest National Laboratory (PNNL) in support of WTP to expand the understanding of filtration behavior for a wider range of HLW types found on the Hanford Site. These tests created a series of composite waste samples using archived tank waste samples selected from the inventory of the 222S building of the Hanford Site to represent eight general waste categories that encompass approximately 75% of the Hanford underground tank waste inventory. The archived 222S samples were originally taken between 1992 and 2002; the majority of the samples were taken between 1995 and 1998. In general, for each waste group, samples were combined into composites, screened to remove or breakup large particles and agglomerates, hydrated and homogenized. Six filtration/leaching tests (see Table 2) were performed using this material (refer to the individual reports for additional details, especially section 2 [4–8]).

The goal was to relate the observed filtration/leaching behavior to the chemical and physical characteristics of the waste slurries tested. As part of this study, filtration flux as a function of time was analyzed to assess the impact of filter fouling on performance. The current paper discusses the results of this analysis.

1.1 Data Analysis Approach

Testing has shown that the filter flux can be typically represented in two stages [9]. In the first regime at low solids concentrations, the filter flux is directly proportional to the pressure drop across the membrane, and the resistance is largely a function of the degree of fouling that has occurred on the membrane. The second regime involving high solids concentrations is generally consistent with concentration polarization. Many concentration polarization models have been developed to describe this behavior [9–14]; however, only a limited number of models have assessed the impact of the interaction between depth fouling and surface fouling [15,16]. The interaction between the fouling mechanisms affects the rate of decay in the filter flux with time.

Consequently, to maintain a certain level of performance, back-pulsing is often used to counteract filter fouling. Planned operation of the cross flow filters for the WTP will involve periodic back pulsing of the system. For non-WTP filtration operations, back pulsing is used with a relatively high frequency, ranging from every second [17] to every minute [18]. Due to the constraints of working with radioactive materials, back pulsing in the WTP cross flow filters is expected to occur every hour to every 12 hours. As such, the transient behavior seen after each back pulse plays a significant role in determining the overall efficiency of the filtration system. To address this transient behavior and the periodic back pulses, a model of the transient behavior has been developed.

Filter permeate flux is represented as:

$$J = \frac{\Delta P}{\mu \left(R_m + R_c \right)} \tag{1}$$

where ΔP is the transmembrane pressure, μ is the liquid phase viscosity, and R_m and R_c are the resistances of the filter membrane and filter solids cake. Daniel et al. [19] derived R_m and R_c using:

$$\frac{dR_m}{dt} = k_m \frac{\Delta P}{\mu} \frac{R_m}{R_m + R_c} \tag{2}$$

and

$$\frac{dR_c}{dt} = k_{c,1} \frac{\Delta P}{\mu} \frac{1}{R_m + R_c} - k_{c,2} R_c \tag{3}$$

where k_m, $k_{c,1}$ and $k_{c,2}$ are arbitrary constants. It has been previously shown that this model works relatively well to describe the filter fouling of metal hydroxide simulants over periods of up to 12 hours between back-pulse events. The intent of this work is to evaluate the capability of this model to describe the filtration performance of actual waste samples.

2. Experimental

The source material for the feeds for these tests and physical properties distributions are provided in Table 1. These eight groups represent ~75 wt% of the materials of interest in the expected feeds to the WTP with respect to leaching (Al, Cr, phosphate, and sulfate) [6].

Table 1. Waste Composite Groups Sources

Group ID	Type	HLW Tank Sample	UDS Mass (gm)	Slurry Volume (mL)
1	Bi Phosphate sludge	B-104, BX-112, T-104	200	1800
2	Bi Phosphate saltcake (BY, T)	BX-110, BX-111, BY-104, BY-105, BY-107, BY-108, BY-109, BY-110, BY-112, T-108, T-109, TX-104, TX-113	330	3660
3	CWP, PUREX Cladding Waste sludge	B-108, B-109, BY-109, C-103, C-104, C-105	290	740
4	CWR, REDOX Cladding Waste sludge	U-105, U-201, U-202, U-203, U-204	310	790
5	REDOX sludge	S-101, S-107, S-110, SX-103	700	2700
6	S - Saltcake (S)	S-106, S-111, SX-102, SX-105, SX-106, SY-103, U-103, U-108	120	840
7	TBP Waste sludge	B-106, BX-109	180	1460
8	FeCN Waste sludge	BY-104, BY-105, BY-106, BY-108, BY-110	250	1830

Overall, the materials for these test were used either separately or in combination with each other based on the need to provide an initial dewatered slurry ~20 wt% undissolved solids (UDS). To achieve this, the total UDS mass of the test slurry needed to be a minimum of 300 grams, based on the minimum operation volume of the test apparatus. Sample groups 1, 3, 4, 6, 7 and 8 were found to contain insufficient UDS mass in each sample to be run separately. Therefore, the waste composite groups were blended as appropriate. Table 2 shows the grouping for each filtration leaching test. Extensive physical and chemical characterization of these composite materials was performed before the material was tested [4–8, 20, 21].

Table 2. Materials Used for Filtration Tests

Test	Test Groups	Waste Group Descriptions
1	5	REDOX sludge
2	6 & 5	S - Saltcake (S) + REDOX sludge
3	1 & 2	Bi Phosphate sludge + Bi Phosphate saltcake
4	3 & 4	CWP, PUREX Cladding Waste Sludge + CWR, REDOX Cladding Waste sludge
5	7 & AY102	TBP Waste sludge
6	8 & AY102	FeCN Waste sludge

2.1 Filtration Equipment

The WTP PTF plans to use porous sintered metal tubes, called cell unit filters (CUFs), for the ultrafiltration processes. The filter feed flows through the inside of the filter element axially while the feed permeate passes through the tube walls radially. The filters purchased for this testing were supplied from the Mott Corporation, using the same specifications for the filters being purchased for the WTP-PTF. The filter elements are 316 stainless steel Mott Grade 0.1 porous media (Mott Catalogue numbers 7610-1/2-24-0.1-AA and 7610-1/2-96-0.1-AA). Bubble point and isopropyl alcohol filter flux data indicate an equivalent pore radius on the order of 1 μm (although the filter material is capable of retaining much smaller particles).

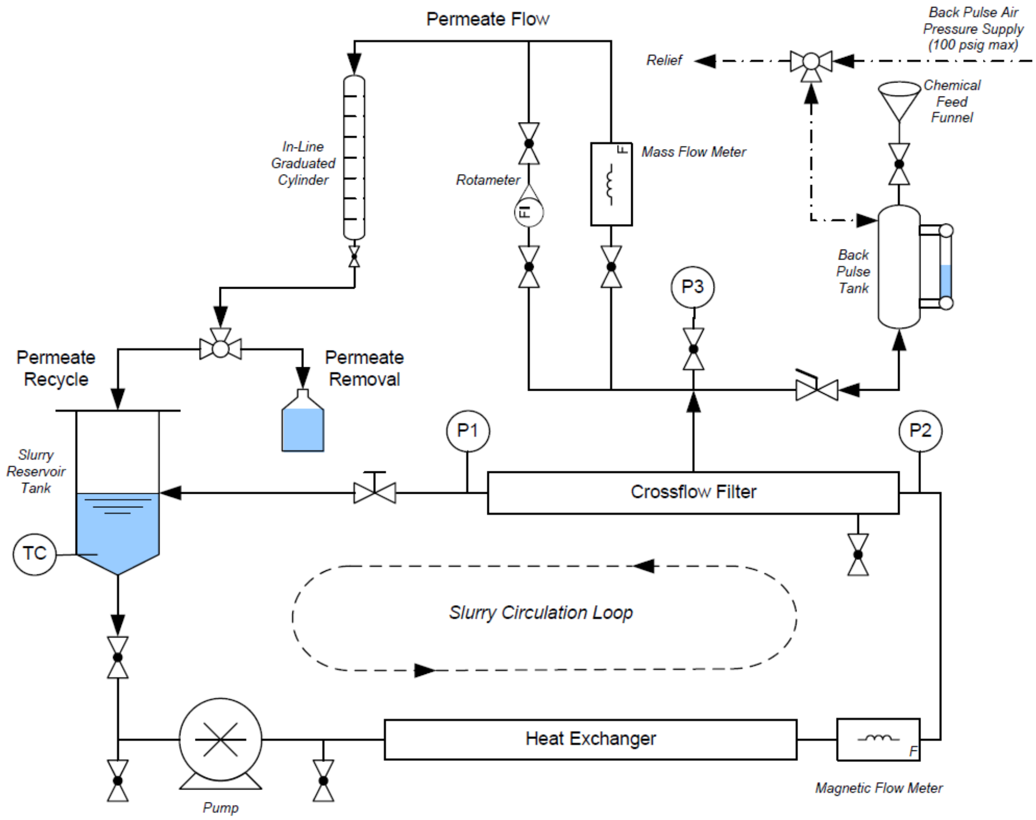

Figure 2. Schematic of the crossflow filter skid used in testing.

A single CUF, 2-feet in length, was installed as part of a filtration/leaching apparatus. The testing apparatus was a bench-top system mounted on a skid that allowed up to 4 liters of a waste solution to be circulated through a tubular filter that can measure filter feed flow rates, filtrate flow rates, system pressures, and temperatures simultaneously (see **Figure 2**). The filter unit has four main parts: a slurry reservoir tank, a slurry recirculation loop with a filter surface area of 0.024 m^2, a permeate flow loop that directs permeate either back to the slurry or to a sample vessel when concentrating the slurry, and a permeate backpulse system capable of delivering an average of 70 mL in 5 seconds. The testing apparatus used a heat exchanger on the main flow loop to remove pump heat and maintain a constant temperature. The system was installed in a hot cell at a PNNL test facility to provide adequate shielding and contamination protection from the waste samples used for these tests.

The waste slurry was circulated through the filtration testing apparatus while the slurry permeate leaving the filter was recycled back to the slurry reservoir. By recycling permeate in this way, the UDS concentration of the slurry remained constant. Using a transmembrane pressure (TMP) of 40 psid and an axial velocity (AV) of 13 fps as the baseline condition, testing conditions were varied to demonstrate how the flux varies as TMP and AV change from the center condition. Table 3 provides the target conditions for each point in the test matrix.

Table 3. Filtration Test Matrix Operating Conditions.

Test number	Duration (hours)	Target TMP (psid)	Target AV (fps)
1	3 +	40	13
2	1	30	11
3	1	30	15
4	1	50	15
5	1	50	11
6	1	40	13
7	1	40	9
8	1	40	17
9	1	20	13
10	1	60	13
11	1	40	13

Each filtration condition was maintained for at least an hour while permeate was recycled back to the slurry reservoir tank. Before test conditions were changed, a back-pulse on the filter was performed to provide the same starting conditions for each test. Typically, the back-pulse occurred after the slurry pressure was below 20 psig and with the back-pulse chamber pressurized to 80 psig. The initial test performed at the baseline condition was performed for a minimum of 3 hours to observe how the filter flux varied with time to track possible fouling due to the waste.

3. Results and Discussion

Table 4 provides a summary of the physical properties of the actual waste samples used in this testing. The majority of samples contained relatively small particles and had supernate viscosities that ranged from 1.5 to 2.6 cP.

Table 4. Sample Physical Properties

Test Group	PSD			Permeate Viscosity (cP)
	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	
Group 5	0.64	2.3	16	1.5
Group 6/5	0.70	2.4	8.6	1.5
Group 1+2	0.52	2.4	9.5	2.6
Group 3+4	1.0	5.2	16	1.5
Group 7	28	81	150	NM*
Group 8	1.6	6.1	29	2.0
*not measured				

Figures 1 and 2 provide examples of the results obtained for the CUF waste tests. Note that for the tests with Group 3-4 material and Group 5 material, the test conditions were adjusted because of experimental difficulties [20, 21].

Equations 2 and 3 can be numerically integrated for a set of input parameters. This numerical integration was done for the parameters for each of these tests. The adjustable parameters for these tests are shown in Table 5. Note that J_o is not adjusted, but is taken as the initial flux for each test.

Table 5. Model parameters for all six filtration tests.

Parameter	Group 1-2	Group 3-4	Group 5	Group 6	Group 7	Group 8
k_m (m^{-1})	0.95	0.43	0.03	1.40	0.92	0.11
k_{c1} (m^{-2})	7.07×10^{13}	0.00×10^{0}	2.45×10^{12}	2.75×10^{13}	8.23×10^{13}	1.13×10^{13}
k_{c2}(s^{-1})	2.19×10^{-4}	4.67×10^{-4}	4.66×10^{-4}	1.74×10^{-4}	2.14×10^{-3}	2.52×10^{-4}
J_o(m/s)	3.10×10^{-5}	2.08×10^{-5}	4.79×10^{-5}	2.08×10^{-5}	2.28×10^{-5}	2.32×10^{-5}
k_{c1} /k_{c2}	3.23×10^{17}	0.00×10^{0}	5.26×10^{15}	1.58×10^{17}	3.85×10^{16}	4.48×10^{16}

These values of the adjustable parameters were developed by minimizing the error function for the integrated model estimate with the actual measured data. The analysis of variance (ANOVA) [22] table for a typical regression (Group 8) is provided in Table 6. Table 6 indicates that the fit is statistically significant and accounts for 96% of the error from this data set. Each of the six waste tests had model fits with similar regression statistics.

Table 6. ANOVA Table for Group 8 test

Source of Variation	Degrees of Freedom	Sum of Squares		Mean Squares		F-Statistic	
Regression	3	SS_R	1.7E-08	MS_R	5.6E-09	F	8118
Error	827	SS_E	5.7E-10	MS_E	6.9E-13	R^2	0.958
Total	830	TSS	1.4E-08				

Inspection of **Figure 3** indicates that the model fits the data well. As time progresses, the model slightly under predicts the permeate flux, particularly for the last few experimental test conditions. However, as the shape of the decay curves for each of these segments appears appropriate, this suggests that the data may slightly over-predict the k_m factor for the later portion of this test. This might suggest that k_m may decrease slightly over the duration of testing for this waste type. Also note that **Figure 3** presents the waste group with the largest value for the ratio of k_{c1}/k_{c2}. This is indicative that the largest decrease in filter flux is associated with the development of surface fouling.

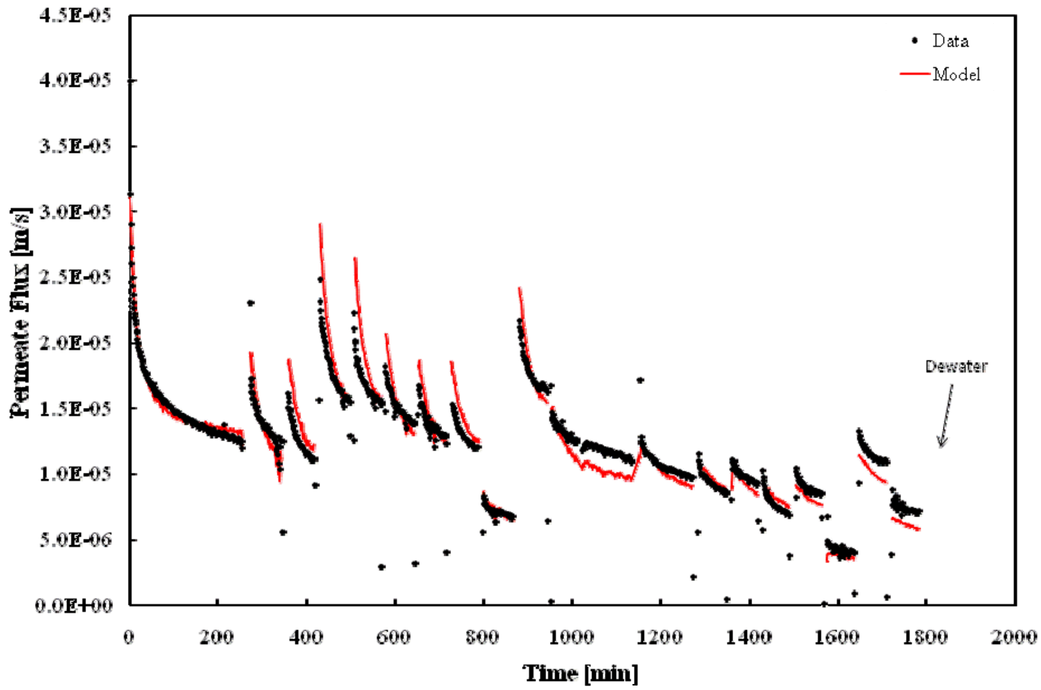

Figure 3. Filter flux data and model results for Group 1-2 test.

A statistically significant fit was obtained for the Group 3-4 data despite a fair amount of noise in the data (due to experimental difficulties [21]). As indicated in Table 3, the best fit to these data was obtained with a k_{c1} value of 0. A zero value of k_{c1} indicates there is negligible surface fouling occurring during filtration.

The results for Group 6/5 provided the largest value for k_m. This can be seen by comparing the initial fluxes for the first and last test condition. These results suggest very rapid depth fouling of the filter element.

Figure 4 provides the data for the Group 8 sample. Similar to the Group 5 data, this set of data is characterized by a relatively low value for k_m, indicating a relatively small amount of depth fouling. Also note that this waste was characterized by a relatively low value for the ratio between k_{c1} and k_{c2}, indicating relatively little surface fouling as well.

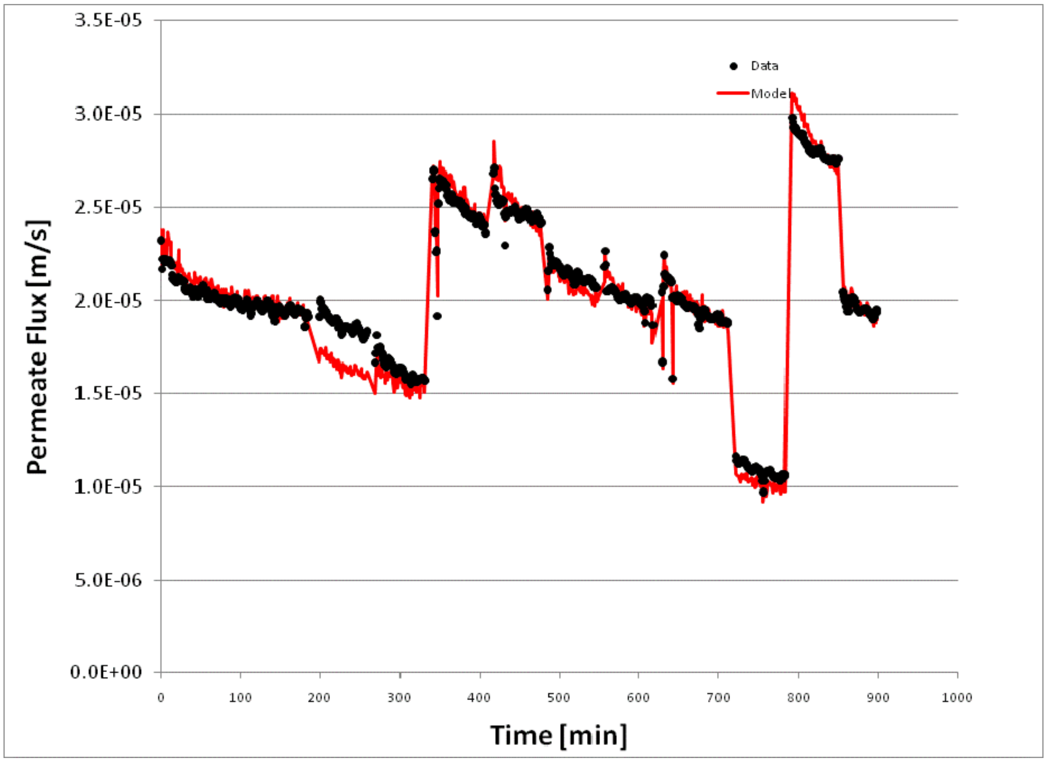

Figure 4. Filter flux data and model results for Group 8 filtration.

4. Conclusions

The data from the actual waste tests were well described by a model given in Equations 1-3. The statistics for these fits were very good. These tests were performed over a range of both pressure drops and axial velocities. The model appears to appropriately account for these variations in process conditions, in particular the pressure drops.

The results indicate a wide range of behaviors for the wastes to be processed by the WTP. Values for k_m ranged from very low (0.03) to fairly higher (1.4). These values correspond to essentially no depth fouling over the 12+ hours of testing to nearly 50% loss in filter flux due to depth fouling. Similarly, there is a relatively large range in the values for the ratio of k_{c1}/k_{c2}. These values ranged from 0, indicating very little surface fouling, to 3.23×10^{17}, indicating significant depth fouling, resulting in a 50% decrease in filter flux over a 3-hour time period.

This wide range of behaviors will result in the need for an adaptive strategy for optimization of filter performance. Selected wastes will be able to operate effectively with essentially no back pulsing and very infrequent cleaning (such as Group 5), while other wastes will require frequent back pulsing and cleaning (such as Group 1-2).

It is important to note that these results do not imply that the WTP flowsheet will not be sufficient to process the waste. They do suggest that there are operational approaches to maximize throughput when filtering different waste types. The model presented herein provides a simple way to predict behavior of waste types and adapt filter operation to process waste as effectively as possible.

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