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FOULING OF CERAMIC FILTERS AND THIN-FILM COMPOSITE REVERSE OSMOSIS MEMBRANES BY INORGANIC AND BACTERIOLOGICAL CONSTITUENTS (U)

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ABSTRACT

Two significant problems have been identified during the first three years of operating the Savannah River Site Effluent Treatment Facility. These problems encompass two of the facility's major processing areas: the microfiltration and reverse osmosis steps. The microfilters (crossflow ceramic filters – 0.2μ nominal pore size) have been prone to pluggage problems. The presence of bacteria and bacteria byproducts in the microfilter feed, along with small quantities of colloidal iron, silica, and aluminum, results in a filter foulant that rapidly deteriorates filter performance and is difficult to remove by chemical cleaning. Processing rates through the filters have dropped from the design flowrate of 300 gpm after cleaning to 60 gpm within minutes.

The combination of bacteria (from internal sources) and low concentrations of inorganic species resulted in substantial reductions in the reverse osmosis system performance. The salt rejection has been found to decrease from 99+% to 97%, along with a 50% loss in throughput, within a few hours of cleaning.

Experimental work has led to implementation of several changes to plant operation and to planned upgrades of existing equipment. It has been shown that biological control in the influent is necessary to achieve design flowrates. Experiments have also shown that the filter performance can be optimized by the use of efficient filter backpulsing and the addition of aluminum nitrate (15 to 30 mg/L Al^{3+}) to the filter feed. The aluminum nitrate assists by controlling adsorption of colloidal inorganic precipitates and biological contaminants. In addition, improved cleaning procedures have been identified for the reverse osmosis units.

This paper provides a summary of the plant problems and the experimental work that has been completed to understand and correct these problems.

INTRODUCTION

The Savannah River Site (SRS) built the Effluent Treatment Facility (ETF) to treat low–level radioactive wastewater. This water comes from three sources: (a) evaporator overheads, (b) contaminated cooling water, and (c) storm runoff. The ETF replaced existing seepage basins as the primary method of wastewater treatment, and began operation in October 1988.

Process Description

The wastewater contains trace quantities of various soluble and sparingly soluble salts. Table 1 gives a summary of the species expected, along with their minimum and maximum concentrations. The predominant species in the suspended solids are iron, aluminum, and silica. Sodium nitrate comprises about 95% of the total dissolved solids (TDS). This waste stream also contains trace quantities of organics, primarily tri–n–butyl phosphate (TBP), and radionuclides.

The ETF was designed to treat the wastestream and concentrate the contaminants for final disposition in an environmentally–acceptable manner. The treated water is discharged through a National Pollution Discharge Elimination System (NPDES)–permitted outfall to a surface water stream. The clean–water discharge criteria to be met include an oil and grease limit (daily maximum = 15 mg/L), a biological oxygen demand limit (daily maximum = 40 mg/L), and limits on all toxic metals (e.g., Cu, Hg, Pb).

The process consists of several treatment steps:

- pH adjustment
- microfiltration (MF)
- mercury removal
- organic removal
- reverse osmosis (RO)
- ion exchange (with regeneration)
- evaporation

The microfilter (MF) step is designed to remove suspended solids above 0.2μ. The purpose of the MF step is to precipitate the majority of the radionuclides on the solids, and to reduce the solute load on the reverse osmosis (RO) process. The RO process removes dissolved solids. The filter and membrane units are composed of three parallel treatment systems or trains (each train is configured with three stages), each with a design capacity of 379 L/min (100 gpm). This configuration gives a maximum flowrate of 1137 L/min (300 gpm). The average required processing rate is 625 L/min (165 gpm). This design strategy was chosen so that routine operation would require two trains in operation, with the third in a standby mode for cleaning or repairs. The concentrated waste material is solidified in concrete grout.

A flowsheet of the process is shown in Figure 1. Granular activated carbon is used for the organic removal process. The first Hg removal column is used to prevent the activated carbon from becoming hazardous waste. The second Hg column is to remove volatile Hg from the evaporator overheads. Several minor unit operations, such as: (a) basket strainers, (b) dechlorination, (c) pH adjustment, (d) cooling steps, and (e) cartridge filters, are also present in the facility.

Microfilter (MF) Fouling Problems

The ETF began operation in October 1988. Several problems were encountered shortly after startup. A major problem was rapid and severe fouling in the microfiltration (MF) step. Treated water flowrates would start at 100 gpm per train, and rapidly drop to as low as 20 gpm. Filter cleaning cycles required up to 18 hours. The rapid fouling and lengthy cleaning cycles have the potential to impact various separation and reactor operations sitewide.

Early analysis of the problem suggested that the fouling was primarily due to inorganic constituents in the feed stream. Specifically, Al(III), Fe(III), and Si(IV) were found to be present in the filter membrane structure. These materials are widely known to cause problems in filtration operations.

Reverse Osmosis (RO) Fouling Problems

The RO units at the ETF have also been plagued with operational difficulties. The system is operated in a constant permeate flow mode, with the feed pressure increased to compensate for any loss in permeate flow. Flux losses are usually due to membrane fouling or increases in feed salt content. Rapid feed–pressure increases, along with poor salt rejection, have often been observed. These problems were thought to be caused by both biofouling and mechanical problems, such as O–ring failures.

EXPERIMENTAL

Description of Experimental Units

Microfilter

The microfilter (MF) studies involved the use of: laboratory–scale, 2 gpm pilot–scale, and 40 gpm semiworks scale filtration systems. Both single lumen and multiple lumen filters (19 single–lumen feed channels) were used in these studies. A diagram of the MF units used is shown in Figure 2. The filters are Norton Ceraflo™ ceramic microfilters. They are composed entirely of sintered aluminum oxide, in which the thin (15μ thick) membrane provides the majority of the hydraulic resistance (the nominal pore size is reported to be 0.2 μ). The filters are operated in the crossflow mode. Figure 3 is a description of the crossflow filtration process. The retained solids build up on the filter surface, and excess solids are swept away with the bulk flow and by periodic backpulsing (which aids in the removal of solids and prolongs the runtimes). The concentrated solution exits the filter element.

Reverse Osmosis

Laboratory-scale and 5 gpm pilot-scale RO units were configured similarly to the MF units. The RO units use Filmtec™ spiral-wound high rejection seawater membranes. These membranes can operate at 90% water recovery and greater than 90% overall salt rejection. The salt removal is accomplished through a combination of convection of solids toward the membrane, and back-diffusion of rejected solids toward the bulk solution. The process is enhanced by the fact that the permeability of water through the membrane is greater than that of the dissolved solids, which leads to the solids content increasing at the membrane surface and creating a driving force for back diffusion.

Experimental Procedure

Microfilter Studies

The solutions used to study the filter fouling problems were simulated ETF influent. Actual influent was not used due to the low levels of radioactivity in the ETF wastewater. The standard simulant used was: 5.7 mg/L Fe(III), 5.0 mg/L Si(IV), 2.7 mg/L Al(III), 1500 mg/L $NaNO_3$. Additional tests were conducted with 5 mg/L Fe(III), and well water. Bacterial tests were run with *Enterobacter cloacae and Pseudomonas sp.*, which are gram-negative encapsulated bacteria, added to the standard simulant concentrations of 10^5 to 10^7 bacteria/mL. The bacteria were cultured by inoculation of a sterile nutrient broth and subsequent incubation. The bacteria were collected by centrifugation.

Simulant solutions were prepared by dissolving $Al(NO_3)_3$, $Fe(NO_3)_3$, and Na_2SiO_3 in 1 to 4 liters of 0.1M nitric acid. The concentrated solution was slowly added to 40 to 45 gallons of either deionized (DI) water or filtered well water. Pretreatment chemicals were added and the solution neutralized to pH = 7.5 with 1.0M or 4.0M NaOH. Bacteria were added (before or after neutralization as desired), and the filtration process started.

The experiments were conducted in both the total-recycle mode (permeate and concentrate returned to the feed tank) and the single-pass (permeate and concentrate discharged to the drain) mode. The filtrate rate and quality, in terms of turbidity and solids content, were monitored with time. The feed transmembrane pressure was typically maintained at 19 to 30 psi, and the backpulsing pressure at 40 to 90 psi. The experimental objective was to maintain a net backpulse pressure of 20 to 30 psi (equal to the feed pressure). The backpulses were performed every 2 to 3 minutes for 2 to 3 seconds. The duration of an experiment was 2 to 20 hours.

Chemical cleaning of the filters involved recirculation of both a hot (40 to 60°C) 2% oxalic acid solution and a hot 2% NaOH and 100 mg/L OCl^- solution. Feed pressures during cleaning were typically 30 psi. Backpulsing was not employed during cleaning. The duration of the cleaning cycles was typically 2 to 3 hours.

RO Studies

The RO experiments were performed differently from the MF studies. The primary difference was that the RO tests involved concentrate recycle and permeate discharge to concentrate the feed solution. This simulated solution traveled along a staged membrane system and allowed RO performance at all water recovery levels to be tested. Reagents and bacteria were initially added to deionized water. The permeate was diverted to drain until 90% water removal (or recovery) was achieved, then the feed tank was refilled and the process repeated for the desired number of cycles. Permeate flow and quality (in terms of salt rejection) were monitored with time. The feed pressure was 400 to 500 psi and the feed rate was 3 to 5 gpm. The experiments were typically 2 to 6 hours in duration.

Chemical cleaning of the membrane involved recirculation of a warm (25 to 30°C) pH = 12 NaOH solution at 200 psi. Operating the cleaning cycle at 200 psi allowed a portion of the cleaning solution to permeate the membrane to affect subsurface cleaning. The duration of the cleaning cycles was typically 2 to 3 hours.

Analytical Methods

Typical analyses performed included conductivity and pH measurements, solids content, and elemental analyses for any species present in the feed. The metals were analyzed by atomic absorption spectroscopy. Bacteria samples were collected in sterile 50–mL centrifuge tubes and fixed by the addition of 1.0 mL of 1.0% formalin. The bacteria concentrations were determined by the Acridine Orange Direct Count (AODC) technique.[1]

RESULTS AND DISCUSSION

Filtration Fundamentals

Crossflow filter performance is dependent upon the degree of solids buildup on the filter surface. Increased solids buildup leads to decreases in the filter permeability and throughput. The formation of a thin surface layer of solids acts as a dynamic membrane layer that rejects small particles that might otherwise penetrate the filter structure.

Solids buildup on the filter surface can be affected by pretreatment of the feed and by mechanical changes to the filter system. Higher feed velocities usually reduce the solids on the filter surface, as does periodically backpulsing the filter. Backpulsing is the application of pressure (via a pump or gas pressure line) on the permeate side to reverse the flow through the filter. Higher values of the ratio of the backpulse pressure to feed pressure typically increase the effectiveness of the backpulse. The reduction of solids levels on the filter surface should result in increased permeate flow and less frequent cleanings.

The presence of Al(III), Fe(III), and Si(IV) in the feed results in the formation of colloidal precipitates in the neutralized filter feed. These small colloidal solids (particles have been measured as small as 0.015μ), have high zeta potentials, and tend to be gelatinous. Particle morphology can be improved by using various neutralization chemicals. Sodium hydroxide is used for neutralization at the ETF, but is also known to form colloidal precipitates. Sodium carbonate, lime, and magnesium hydroxide are often used to improve particle crystallinity and filterability. Particle morphology can also be improved by heating (digesting) the solution prior to filtration. Heat dehydrates the colloidal particle flocs and results in denser particles, but this solution is impractical due to the energy requirements for a large feed stream.

A large variety of organic polymeric flocculating agents exist that can be used to improve the solids character. These are often used in clarifiers and multimedia filters. Also, various solids, such as powdered activated carbon and diatomaceous earth, can be used as bodyfeeds. The bodyfeed introduces a surface for adsorption of the colloidal particles and therefore should improve solution filterability. Erosion of pumping and piping hardware must be considered for this approach. Additionally, this significantly increases the amount of secondary waste generated due to the higher solids content.

Another approach, similar to the bodyfeed concept, is to utilize aluminum sulfate (alum), which forms large particles, during neutralization. Alum is widely used for solution enhancement due to its ability to form large, easily-filtered solids that adsorb small solids. Aluminum nitrate also functions in this manner.

Microfilter Studies Involving Biological Constituents

The bacteria tests were initiated after a good correlation was noted between MF performance and the bacteria levels at the ETF. In general, poor performance (60% flux loss) occurred when the bacteria concentration exceeded 1.0E6/mL. The variability in filter feed composition also resulted in poor performance at lower bacteria levels, but in general, high bacteria concentrations resulted in poor filter performance.

The filter tests with bacteria-containing simulants were performed with a single-lumen Norton ceramic microfilter. A single-lumen unit was chosen for these tests in order to have 3 to 5 hours of fresh feed from a 45-gallon batch. The results of the bacterial tests are summarized in Table 2. J/Jo is the normalized permeate flux, which was measured after 30 minutes and at the end of the filter test.

Baseline tests were conducted in the laboratory to confirm the bacterial effects on filter performance. Two concentrations of bacteria were chosen, 0.9×10^5 and 1.0×10^7 bacteria/mL. These levels are typical of the high and low concentrations that are observed at the ETF. The bacteria were added to deionized water at neutral pH, mixed for 10 to 15 minutes, and filtered. The results are shown in Figure 4. No fouling was observed with the 0.9×10^5 bacteria/mL solution during the three hour test. Assuming that the bacteria are roughly 0.5μ in diameter and 2.0μ in length, and the filter has a surface area of 118 cm^2, it should take approximately 11 hours to deposit a monolayer of bacteria on the filter surface. Therefore, no significant effect would be expected from the bacteria in this test. Tests with 1.0×10^7 bacteria/mL resulted in severe and rapid fouling of the filters. Over 40% of the initial flux was lost in 30 minutes, and over 70% in 90 minutes. In this case, the time necessary to deposit a monolayer of bacteria was estimated to be 6 to 7 minutes.

Additional tests were completed to examine combination effects of bacteria and inorganics on filter performance. The results of the filter tests with the standard simulant and bacteria are shown in Figure 5. At bacteria concentrations of 10^5/mL, the filter lost 20% of its initial flux after 20 minutes and 30% after 4 hours. This result compares favorably to the results of filter tests with only inorganic simulants. Because of the low bacteria concentration, not much effect would be expected. However, at a bacterial concentration of 1.0×10^7 bacteria/mL, the filter showed severe and rapid fouling, with a 40% flux loss after 30 minutes and 65% flux loss after 2 hours.

Several treatment methods were examined to remediate the biofouling problems. These included: killing the bacteria by exposure to nitric acid or by boiling, lysing the bacteria with caustic or ozone, and addition of aluminum nitrate to the feed.

Tests were performed to examine the effects of nonculturable (dead) bacteria on filter performance. Since the bacteria were nonculturable, they cannot secrete polysaccharides and would be expected to be less adhesive. Two methods were employed to kill the bacteria: exposing them to 0.03M HNO_3 for one hour or boiling them in water for one hour. The standard simulant was used for each of these tests.

The results with acid-treated and heat-treated bacteria are shown in Table 2. Both treatment methods were effective at killing the bacteria. However, as can be seen in the table, the filters still fouled very badly, losing 65 to 70% of their initial flux within a few hours. These results demonstrate that even though the bacteria were nonviable, the intact cells still caused severe and rapid fouling of the filters.

The results with lysed bacteria are also shown in Table 2. Exposing the bacteria to 0.25M NaOH for 21 hours reduced the bacteria concentration by 99%. However, when this simulant was filtered, the filter lost 45% of its initial flux after 90 minutes. This fouling was more rapid and severe than when the simulant contained only inorganics, but it was not as severe as when the simulant contained intact bacteria. Exposing the bacteria to UV–ozone for 12 hours reduced the bacterial concentration by over 95%. Again the filter fouled very rapidly, losing 70% of its initial flux after 90 minutes.

In these tests, significant fouling was observed despite the lack of intact cells. This fouling can be explained as being due to the physical adsorption of a matrix of biological macromolecules and inorganic colloids onto the alumina substratum. The intracellular and extracellular components which are released into the solution upon lysing can adhere strongly to the surface. In particular, adhesive excretory polymers such as polysaccharides make up a large fraction of the material surrounding encapsulated bacteria, such as *Enterobacter cloacae and Pseudomonas sp.*

From the results presented above, it is obvious that killing or lysing the bacteria will not improve the filterability of bacteria–containing feeds. Since $Al(NO_3)_3$ addition has been shown to improve the filterability of inorganic simulants (which will be discussed later), $Al(NO_3)_3$ addition was tested to improve the filterability of bacteria–containing feeds.

Noticeable improvements in filter performance were observed with aluminum(III) nitrate addition to the simulant containing 1.0E6 bacteria/mL, as shown in Figure 6. The filter experienced only a 30% flux loss after three hours. Contrast this to 65% flux loss in two hours in the absence of $Al(NO_3)_3$. This is comparable to the filter performance with inorganic simulant alone. During the test, large changes were observed in the permeate backpressure and flowrate between backpulses (3 to 7 psi, 0.00 to 0.05 L/min). This demonstrates that good backpulsing is imperative if this treatment method is to be employed.

In all of these tests, the Norton ceramic microfilters are effective at removing the bacteria from the simulant. The concentration of bacteria in the filter permeate is consistently less than 9.00×10^4 bacteria/mL, which is the detection limit in the AODC method used here.

Microfilter Cleaning Studies

Several improvements were also made in the filter cleaning procedures at the ETF. Initially, the filters were cleaned with 2% nitric acid. Marginal improvements in permeate flux resulted. The use of a 2% oxalic acid solution at 40 to 50°C restored a large portion of the flux loss. The oxalic acid is thought to be removing the iron which fouls the filters. A solution containing 2% NaOH and 100 to 150 mg/L OCl^- at 40 to 50°C was recommended by the vendor to remove the biofouling. This combination of cleaning solutions was shown to be effective in restoring filter performance on the pilot- and laboratory-scale units when processing inorganic simulants.

Cleaning tests at the ETF showed that the filters would appear clean when processing well water, but would rapidly foul when processing actual feed. This phenomenon was also noted with the laboratory-scale unit when bacteria-containing solutions were tested. It was found that bacteria-fouled filters needed to be boiled in the oxalic acid and $NaOH/OCl^-$ solutions. Research is ongoing pertaining to this phenomenon.

Microfilter Studies Involving Inorganic Constituents

Although the primary problem with the Norton filters has been biofouling, fouling due to colloidal inorganic precipitates has also contributed to the problem. Studies were completed to improve the filter performance by adjustment of the feed pretreatment chemistry and mechanical changes to filter operation.

The pretreatment chemicals, lime, Na_2CO_3, and Na_3PO_4, were evaluated as alternate neutralization reagents. Polymeric flocculating agents, specifically Betz™ polymers, heat digestion, and aluminum nitrate, were also evaluated.

Various physical methods of improving filter performance were studied. Variations in the frequency, duration, and strength of the backpulse; the feed crossflow velocity; and the filter pore size were examined.

Pretreatment Chemistry

The various pretreatment strategies tested for improving the filter performance at the ETF are summarized in Table 3. Typical starting fluxes were 700 gallons per square foot per day (GFD) at 30 psi transmembrane pressure (TMP). The standard NaOH neutralization resulted in flux losses of up to 50%. The relative improvement data given in Table 3 are a ratio of the filtrate flow for a given pretreatment to the filtrate flow for standard neutralization (both values are taken at t = 18 hours). The majority of pretreatments tested gave little (perhaps 20%) improvement in the filter performance. In some cases performance actually worsened by up to 80 to 90% flux loss (for the case of Betz™ polymer addition).

The most significant result occurred with addition of $Al(NO_3)_3$ to the feed prior to neutralization. Addition of 67.5 to 100 mg/L Al(III) reduced the flux loss from 50% to 10 to 20% (see Figure 7). Higher flux losses were observed when the Al(III) concentration was increased to 135 mg/L. This was probably due to large quantities of feed solids blinding the filter. However, the filter performance with 135 mg/L Al(III) was still better than the performance in the absence of additional Al(III). Thus the addition of Al(III) appeared to be a workable improvement to the filter process, and could substantially improve operations at the ETF.

It is postulated that the beneficial effects of Al(III) addition are due to an electrostatic interaction between the $Al(OH)_3$ precipitate and the colloidal solids in the waste. The resulting $Al(OH)_3$ floc is not attracted to the alumina filter surface and thus acts as a bodyfeed which can be easily backpulsed. Filter performance improves, due to the formation of more easily-filtered solids. One operating concern for using aluminum addition is whether the feed composition of th' stream must be known to determine the amount of Al(III) needed. The need to know the feed composition prior to addition would render the process unfeasible, as the influent stream continually changes composition. Test results showed that the filter performance was the same for a solution of 67.5 mg/L Al(III) and filtered well water (very low iron and silica content) as that obtained for the ETF simulant containing colloidal iron and silica. Thus, Al(III) can be metered into the feed based on the feed rate (easily measured) and not based on the feed composition (difficult to determine in a timely fashion).

The addition of $Al(NO_3)_3$ is pH-sensitive. The preneutralization pH after Al(III) addition must be less than 2.7 to minimize the formation of small colloidal particles. Also, the neutralization pH must be controlled to 7.5 ± 1.0 to optimize precipitate formation. Filtration of a solution that was neutralized to $pH = 6.4$ resulted in filter performance similar to that obtained without Al(III).

Initial testing at the ETF indicates that the addition of Al(III) to the ETF influent does produce improvements in the filter performance. Figure 8 is a summary of the results. A baseline case with normal filtration of a caustic-neutralized feed was established. Four tests were conducted at the ETF with elevated Al(III) concentrations (15 mg/L) in the feed. It can be seen that the performance in all cases was better than that observed for the base case. It can be seen that large drops in performance can occur due to upsets in the pH of the filter feed solution. These upsets were caused by poor pH control in the system and are unrelated to the filter operation. The low influent pH conditions ($pH < 6$) caused formation of large amounts of colloidal solids that rapidly fouled the filters. This condition can be avoided with improved pH control.

Mechanical Improvements

At the ETF, the filter feed is pressurized to 75 psi and the filter concentrate exits the system at 45 psi. An average pressure of 30 psi is maintained on the permeate side for an average transmembrane pressure of 30 psi. The maximum backpulsing pressure is 90 psi. Figure 9 is a description of the process. The result is that, during a backpulse, the region of the filter experiencing the highest fouling (i.e., the entrance region) has only 15 psi of net backpulse pressure, while the downstream end is backpulsed at 45 psi. Therefore, very little backpulsing occurs where it is most needed. Hence, most of the solids are not removed from the filter, and thus filter performance deteriorates rapidly with time.

Tests were conducted to study backpulsing and optimize the backpulse process. Early tests indicated that a backpulse duration of 3 seconds removed the majority of the solids.

This duration was used in all subsequent tests. The backpulse frequency was less important than the backpulse strength (see Figure 10). Little difference was noted when the filter was backpulsed for 3 seconds every 2 hours or every three minutes when using a backpulse to feed pressure ratio (BP/FP) of 1.5. The flux loss in both cases was about 30%. A BP/FP of 1.5 means that the net backpulse pressure (backpulse pressure minus feed pressure) is 50% of the transmembrane pressure, which is approximately the same conditions at the ETF. Increasing the BP/FP to 3 restored a large portion of the flux loss, and gave similar performance to setting the BP/FP to 3 from the start. A BP/FP ratio of 3 resulted in only a 10% loss overnight. The phenomenon of low flux loss with stronger backpulses has been noted before.[2] These researchers noted that increasing the BP/FP to 6 to 12 resulted in very little fouling.

Two methods were examined at the ETF to improve the BP/FP ratio: reducing the feed pressure to the filters, or increasing the backpulsing pressure. An orifice plate was installed in the feed line to one of the filter trains. The orifice plate reduced the effective feed pressure at the filters to 60 psi, and increased the operating filter permeability 50%. Longer run times and shorter cleaning cycles were achieved. Further system upgrades, such as increasing the available backpulsing pressure, are being investigated.

Another improvement that was examined was increasing the filter pore size. It was suggested that a coarser filter would not be fouled by small particles and would have a higher intrinsic permeability. Smaller filters were not tested, as the filter permeability drops substantially for filters rated below 0.2μ. A summary of these tests is shown in Figure 11. Increasing the pore size to 1.2μ resulted in substantial improvements in performance. The flux loss was reduced from 50% to 15 to 20%. The reduced flux loss was due to the higher intrinsic filter permeability and more efficient backpulsing of the 1.2μ filter. The 1.2μ filter experienced large (50%) flux losses between backpulses, which means that the backpulse process is even more crucial to the filtration process. Increasing the pore size to 5μ resulted in catastrophic filter failure, with an immediate loss of 60% in flux, and eventual decay to only 15% of the initial value. A small test unit containing 1.0 to 1.2μ filters is being installed at the ETF for further evaluation.

Additional tests focused on the filter feed velocity. The filters are operated at Re values of 4,000 to 6,000, which is in the transition range between laminar and turbulent flow. Higher feed velocities were tested that corresponded to Re values of up to 12,000. Significant improvements were not observed over the Re values studied.

Reverse Osmosis Studies Involving Biological Constituents

The profound impact of bacteria on the MF process at the ETF prompted tests to quantify the bacteriological effect on the RO membranes. The presence of bacteria in the RO feed can affect water throughput and salt rejection. It has been postulated[3] that the presence of a biolayer on the membrane surface reduces the back-diffusion of salt away from the membrane surface. Hence, the salt concentration at the surface is higher, which means that more salt is convected into the membrane pores, and salt rejection decreases. Also, the biolayer can result in an increased flux loss, and thus result in higher RO feed pressures to maintain the throughput. Higher feed pressures tend to compress the biolayer, thus reducing the overall permeability and aggravating the problem.

Preliminary test results on the RO biofouling are summarized in Figure 12. It can be seen that the first batch of bacteria had no effect on the membrane performance. The rejection values were very similar to those obtained for the bacteria-free solution. Also, the water flux was the same in both the salt and salt-plus-bacteria tests. Significant decreases in salt rejection occurred upon processing the second batch of bacteria. Rejection losses of over 1% occurred, which translates into substantial decreases in the overall efficiency of the RO process. These results were reproduced in subsequent bacteria/salt tests. These rejection losses could mean that high feed concentrations of salt could result in the ETF's inability to meet its discharge criteria.

Higher bacteria concentrations (10^9 bacteria/mL) were tested in order to simulate long-term (one month) bioaccumulation on the membrane. The biofouling that was observed at the 10^7 bacteria/mL level did not exist when a salt solution containing 10^9 bacteria/mL was processed. It appears that the bacteria were clumping together and not adhering to the membrane surface. The phenomenon of bacteria clumping in clean water is well known.

Subsequent testing with bacteria-free salt solutions resulted in substantial flux loss. This was particularly true at higher water recoveries. Approximately 10 to 15% additional flux loss was noted. Although flux loss was observed, no loss in salt rejection occurred in the test following the bacteria. The flux loss was easily restored by washing the membrane with DI water at 200 psi.

Additional results obtained with unused membranes indicate that biofouling can severely affect membrane performance. The membranes are shipped in a 1 to 2% sodium bisulfite preservative solution. This solution has a limited shelf life, and the membrane in these tests had been stored for 2 to 3 years. The loss of preservative in the membrane will result in biological activity on the membrane. The initial salt rejection with 2000 mg/L NaCl of this membrane module was about 98%, whereas the standard rejection should have been $99.3 \pm 0.2\%$. The rejection loss noted was probably due to bacteria, since the membrane had not been exposed to any solution other than salt water. Cleaning the membrane with 0.1% NaOH at 30°C (the ETF cleaning protocol) was unsuccessful. The salt rejection remained unchanged at 98%. Similar results were obtained for a pH = 2 nitric acid solution and a 2% oxalic acid solution.

The performance of this new membrane module was restored by cleaning with an 8 g/L solution of Filmtec™ Alkaline Cleaner at 200 psi and 35°C. This solution contains polyphosphates, sodium metasilicate, and surfactants, and is recommended by Filmtec for removing biofilms. The salt rejection for NaCl after using this cleaner was 99.5%. This membrane was left idle for about six months following this cleaning, and again the NaOH, nitric acid, and oxalic acid were ineffective; once again the Filmtec™ Alkaline Cleaner was required to restore the membrane. The use of the Filmtec™ Alkaline Cleaner is being incorporated into the cleaning procedures at the ETF.

The results indicate that biofouling is indeed a problem for the filters and membranes at the ETF. Additional research is ongoing to investigate remediation processes for the RO biofouling.

SUMMARY AND CONCLUSIONS

Research has been conducted in support of microfilter (MF) and reverse osmosis (RO) fouling problems at the Effluent Treatment Facility (ETF) at the Savannah River Site (SRS).

The MF fouling problems have been found to be twofold, with an inorganic colloidal precipitate problem and a biofouling problem. The biofouling problem was shown to be more severe. The addition of aluminum nitrate (approximately 15 to 30 mg/L Al[III]) to the MF feed prior to neutralization improves the filter performance by controlling adsorption of both colloidal inorganic precipitates and biological contaminants. Filter cleanings are more efficient as a result. Efficient backpulsing also improves the MF process functions and is especially important when using aluminum nitrate addition to the feed.

The RO fouling was found to be primarily due to biofouling. Methods to control this problem are currently being investigated. The RO membranes can be effectively cleaned and restored to prebiofouled conditions with 8 g/L of Filmtec™ Alkaline Cleaner processed at 200 psi and 35°C.

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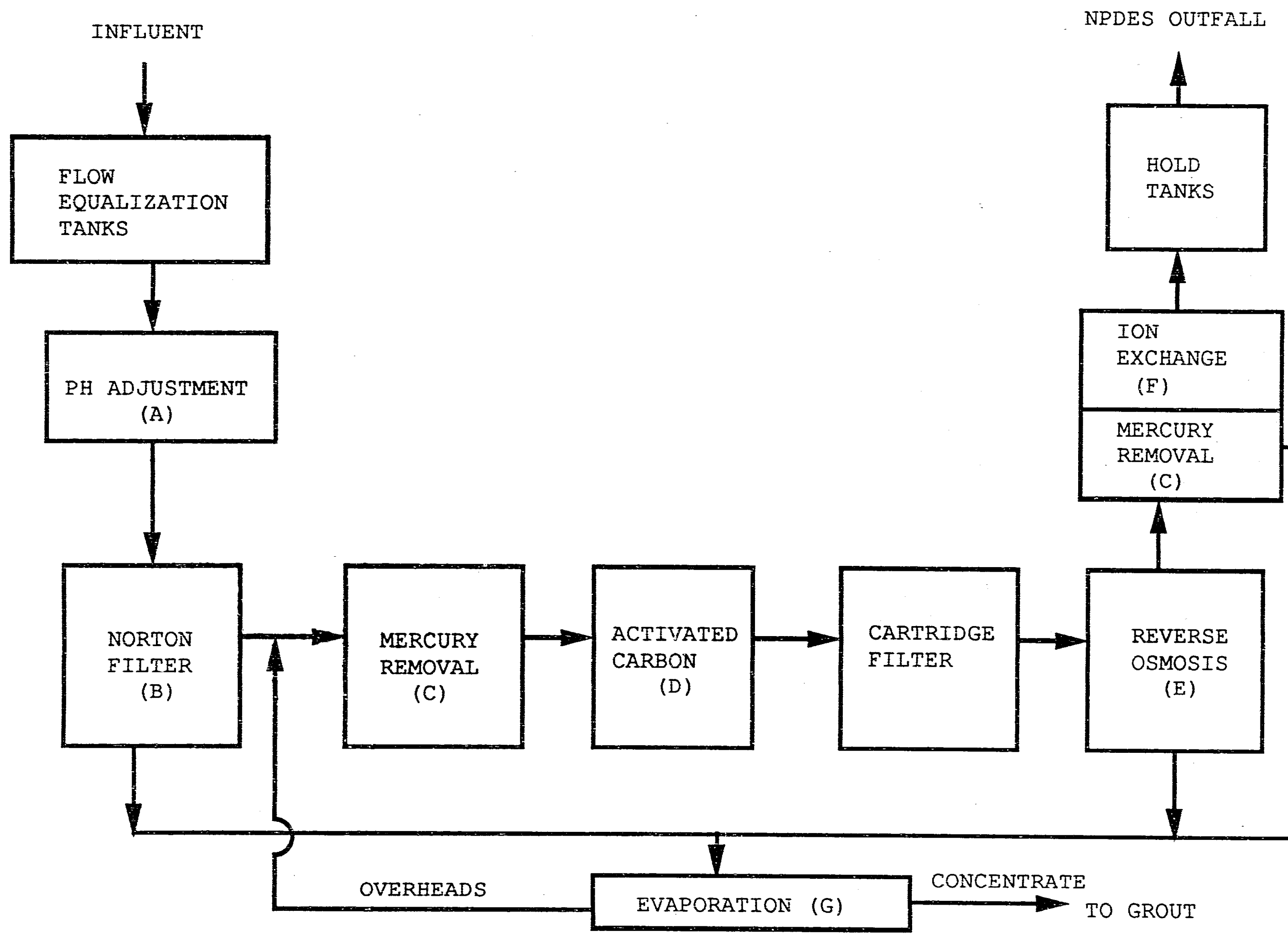

Figure 1. Diagram of the Effluent Treatment Facility

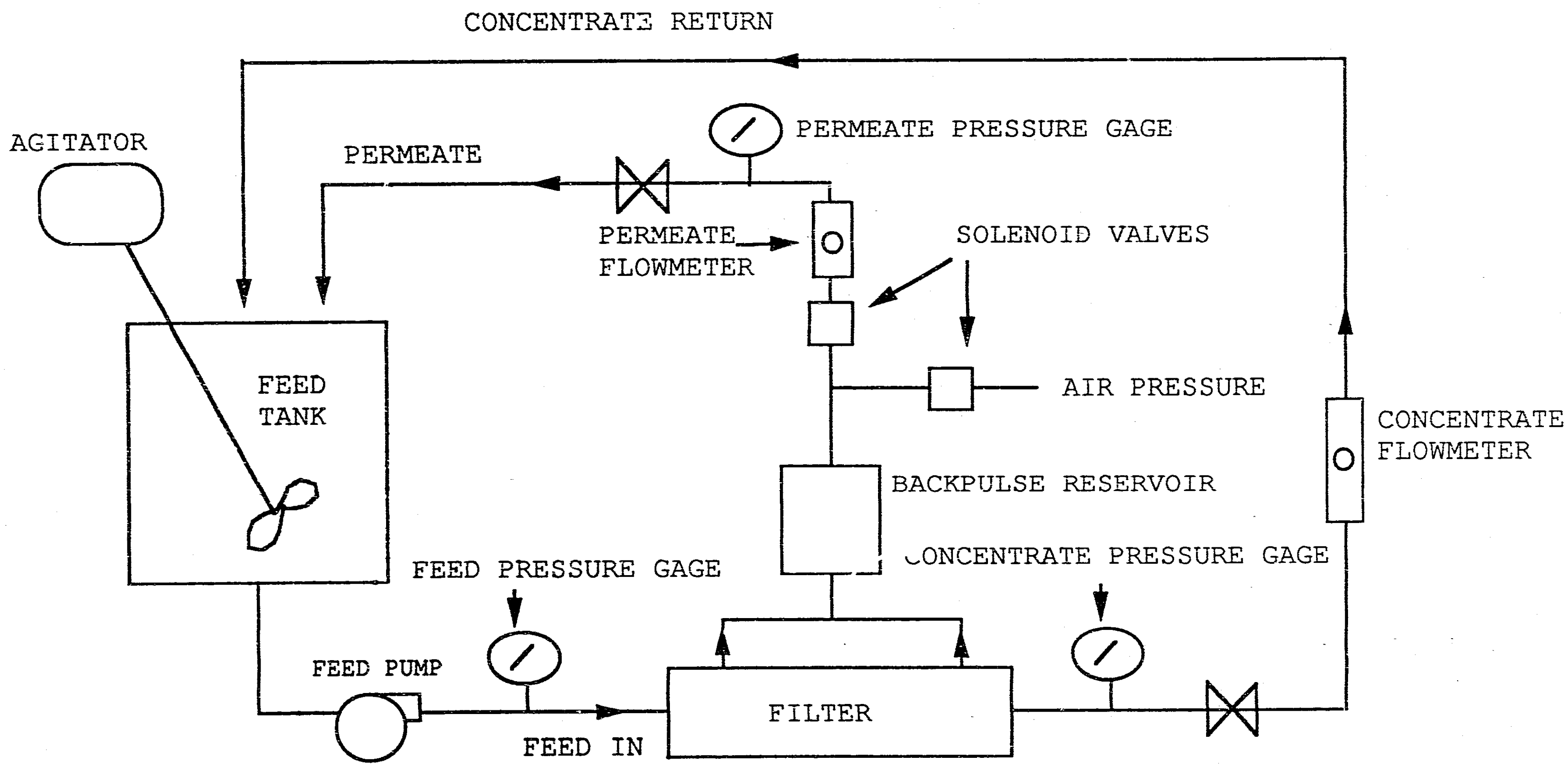

Figure 2. Schematic Diagram of the Experimental Microfilter Unit

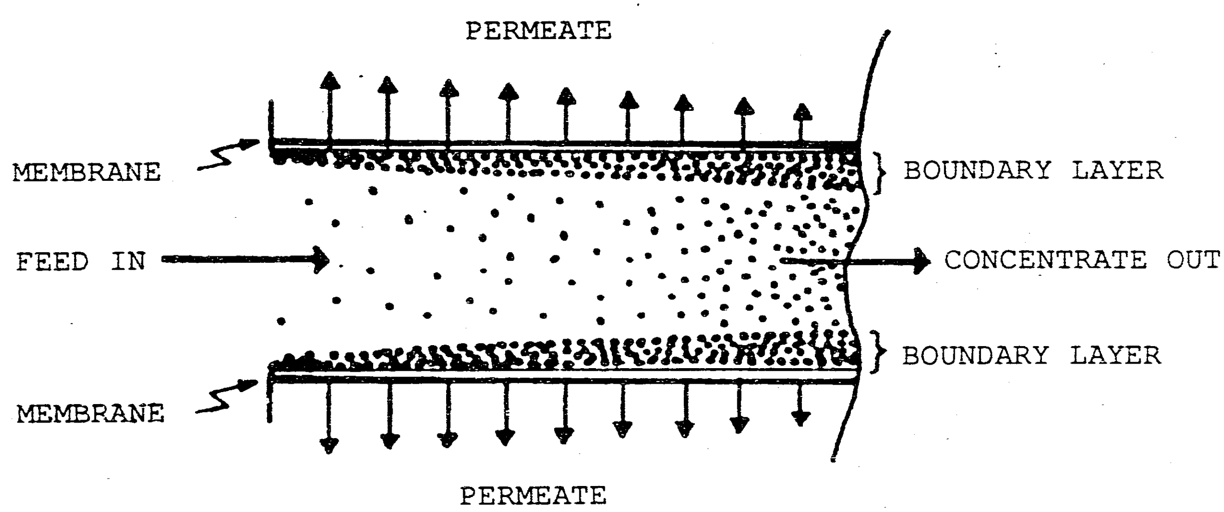

Figure 3. Diagram of the Crossflow Filtration Process

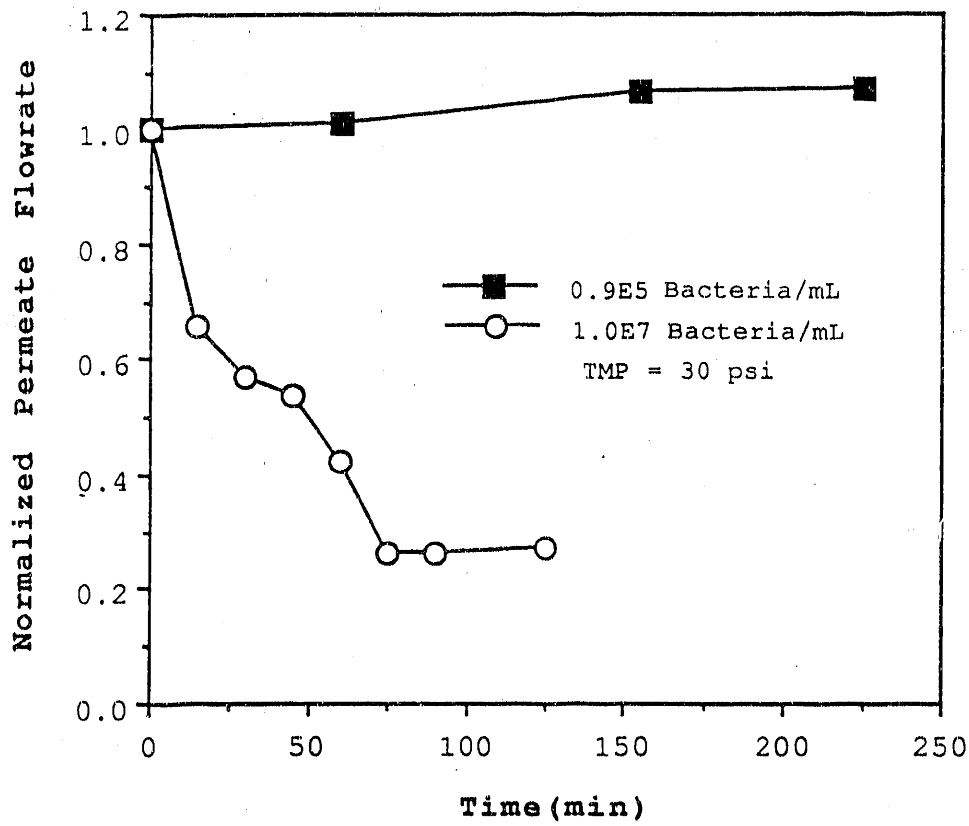

Figure 4. Effect of Bacteria Content on Filter Performance

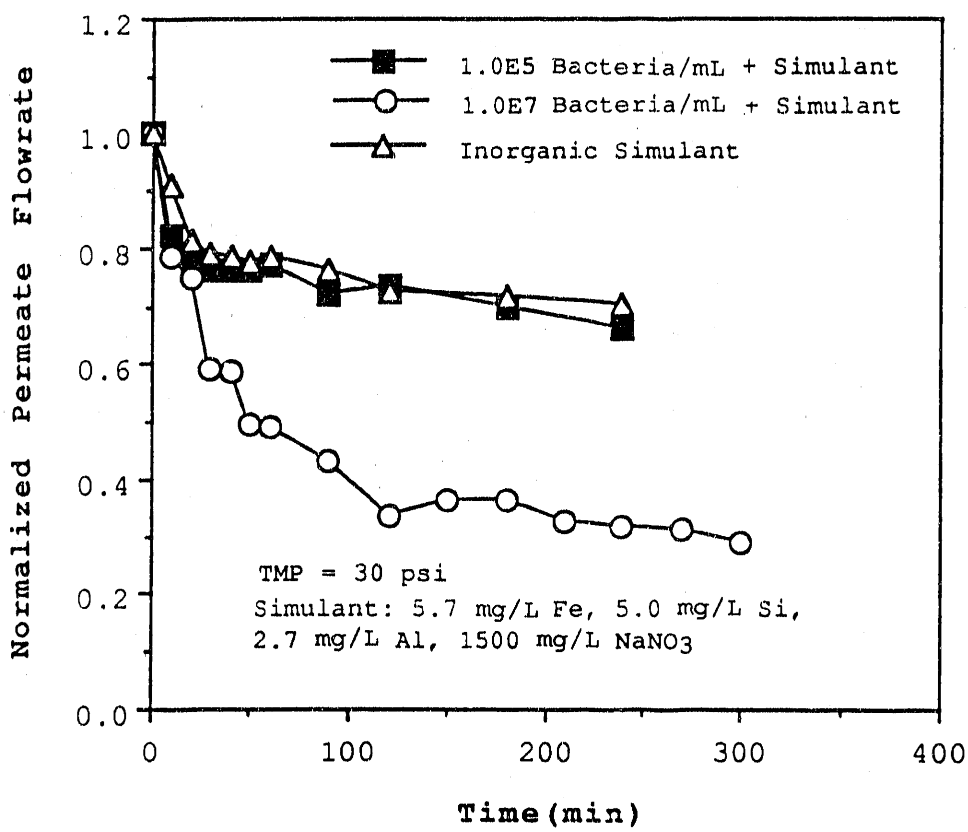

Figure 5. Effect of Bacteria and Inorganics on Filter Performance

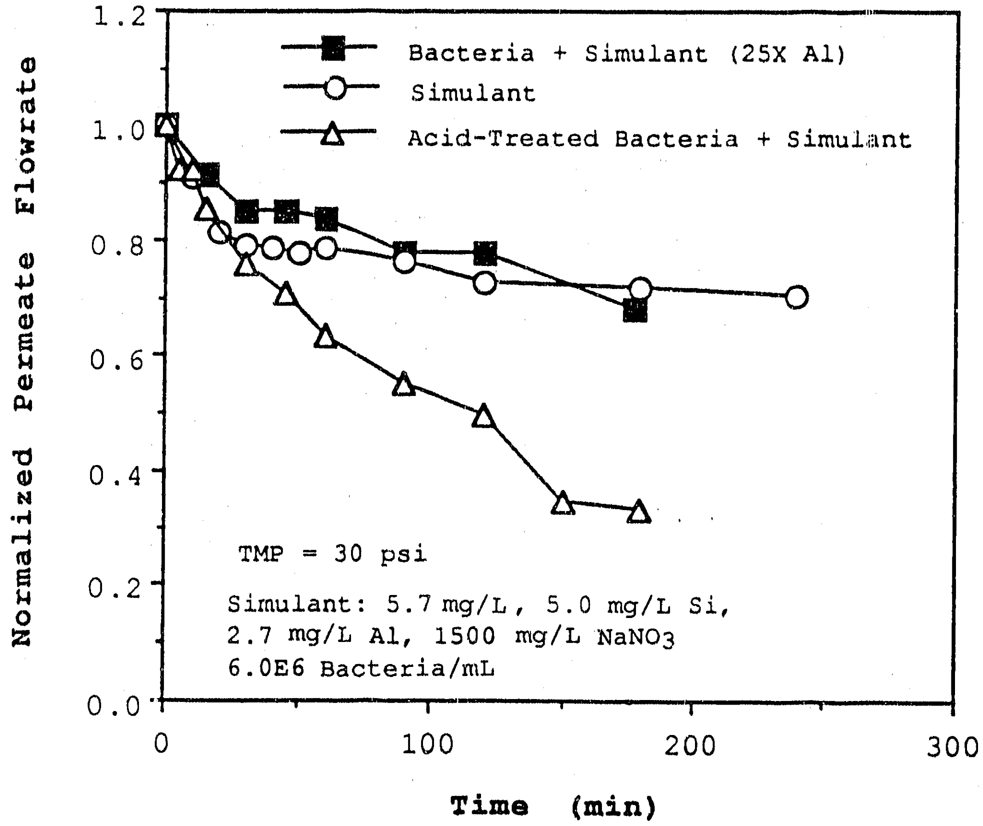

Figure 6. Improvements in the Filterability of Bacteria–Containing Feeds as a Result of Al $(NO_3)_3$ Addition

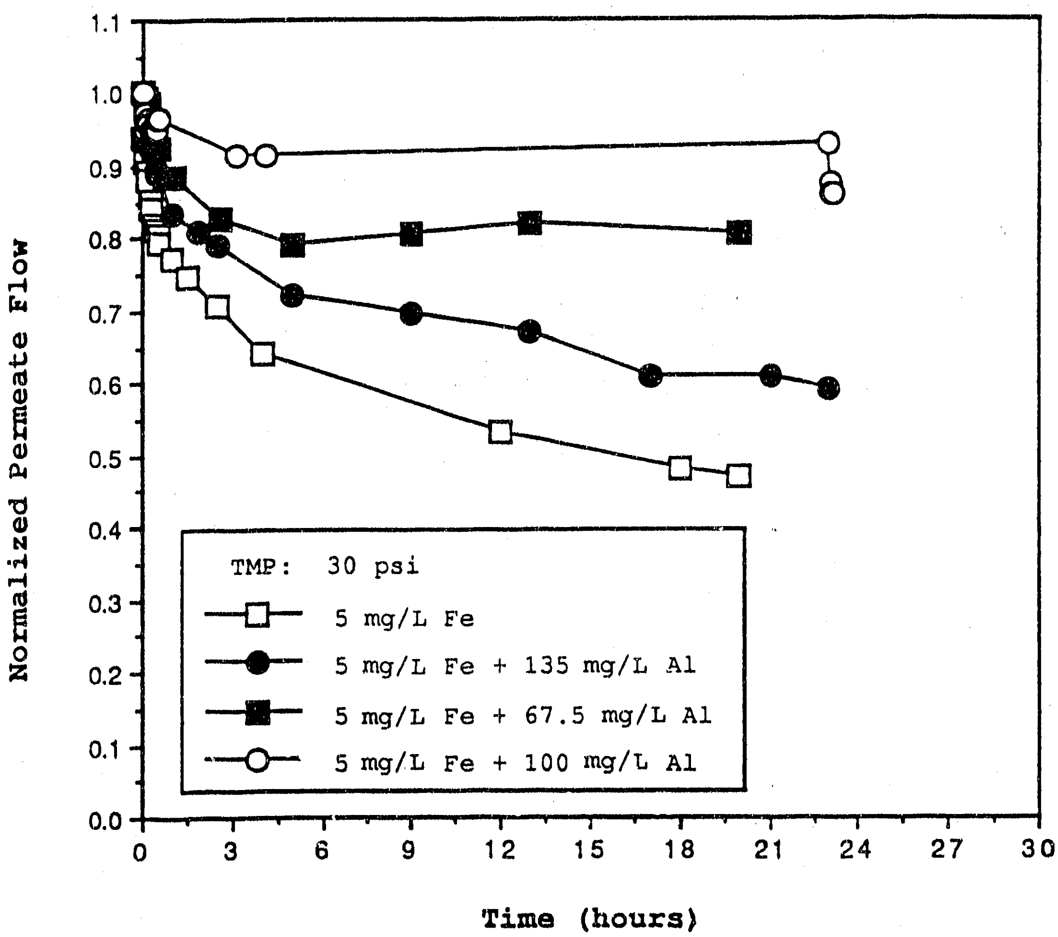

Figure 7. Filter Performance Improvements Resulting from Aluminum Nitrate Addition

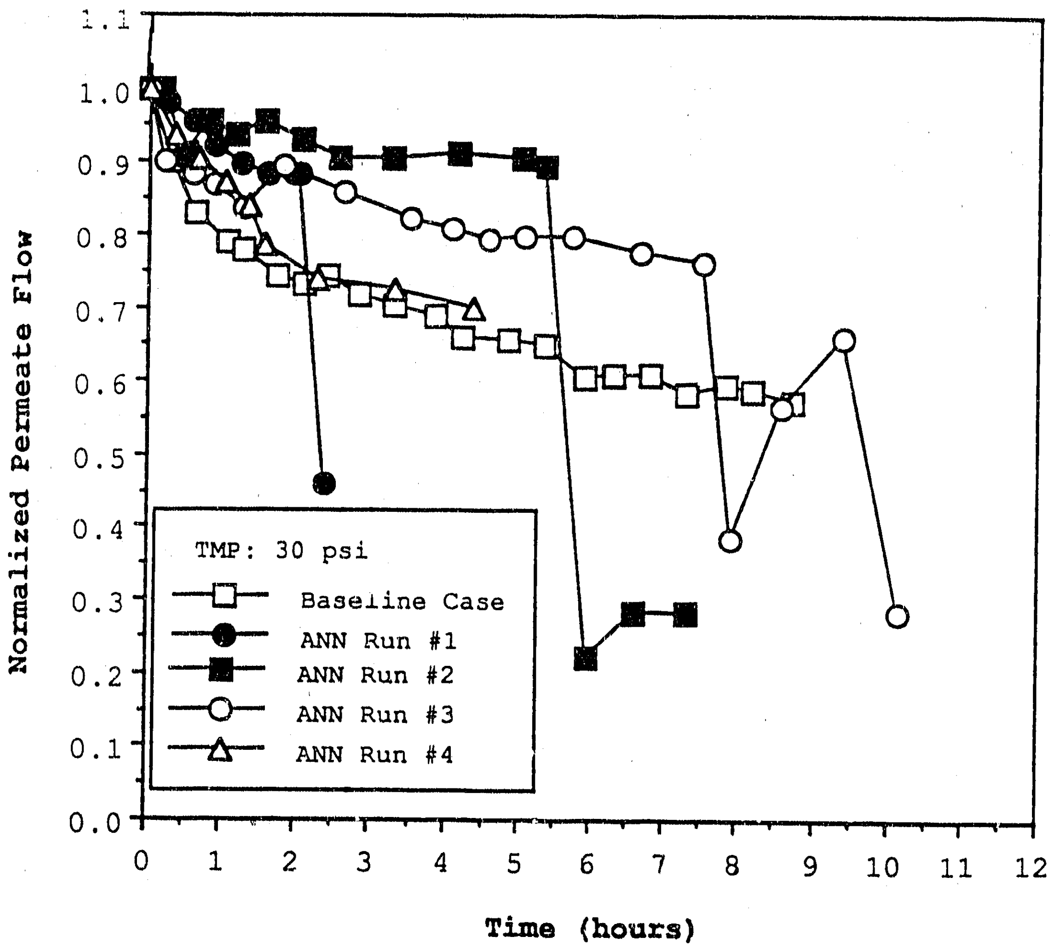

Figure 8. Effectiveness of Aluminum Nitrate Addition

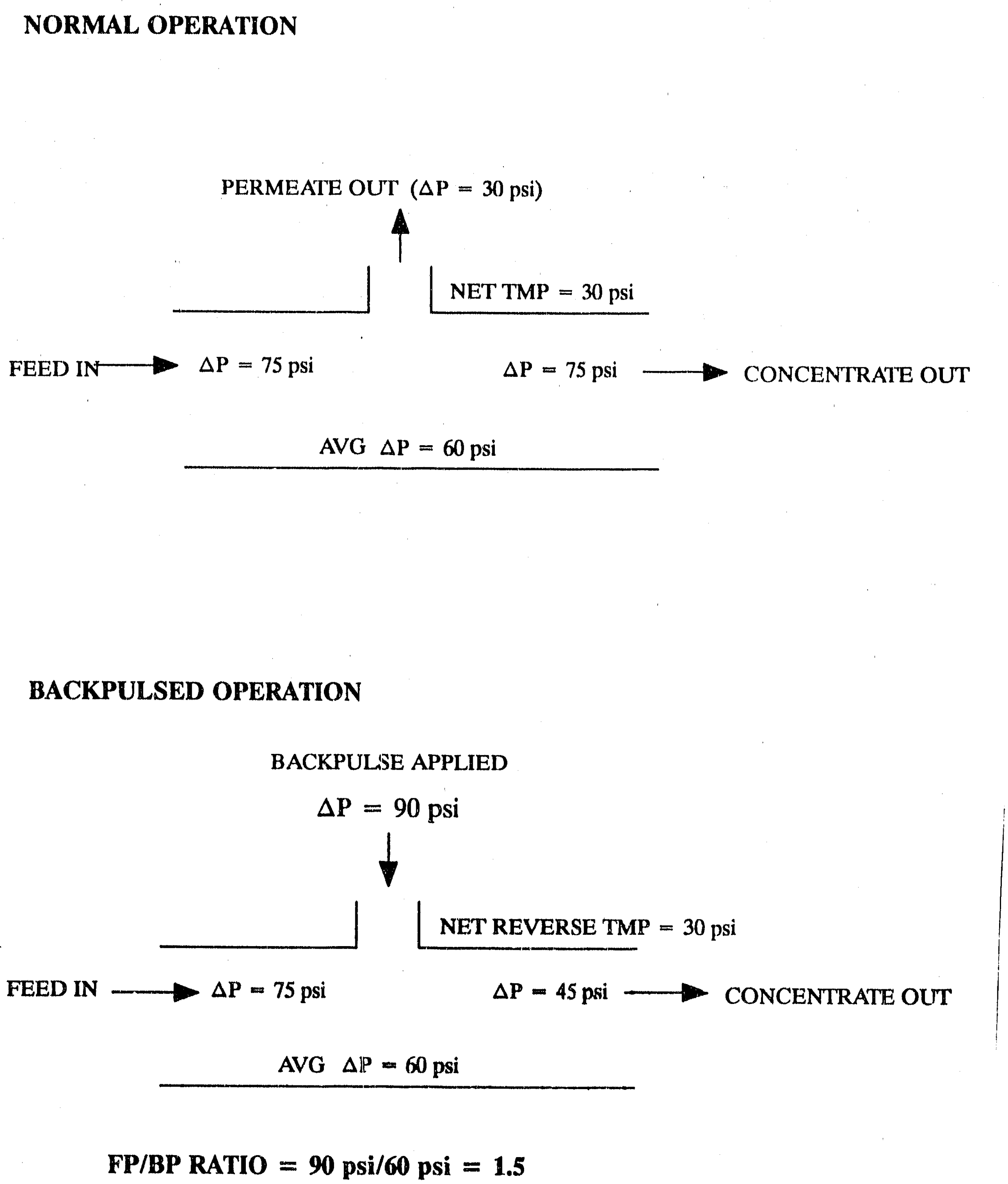

Figure 9. Diagram of the Backpulse Process

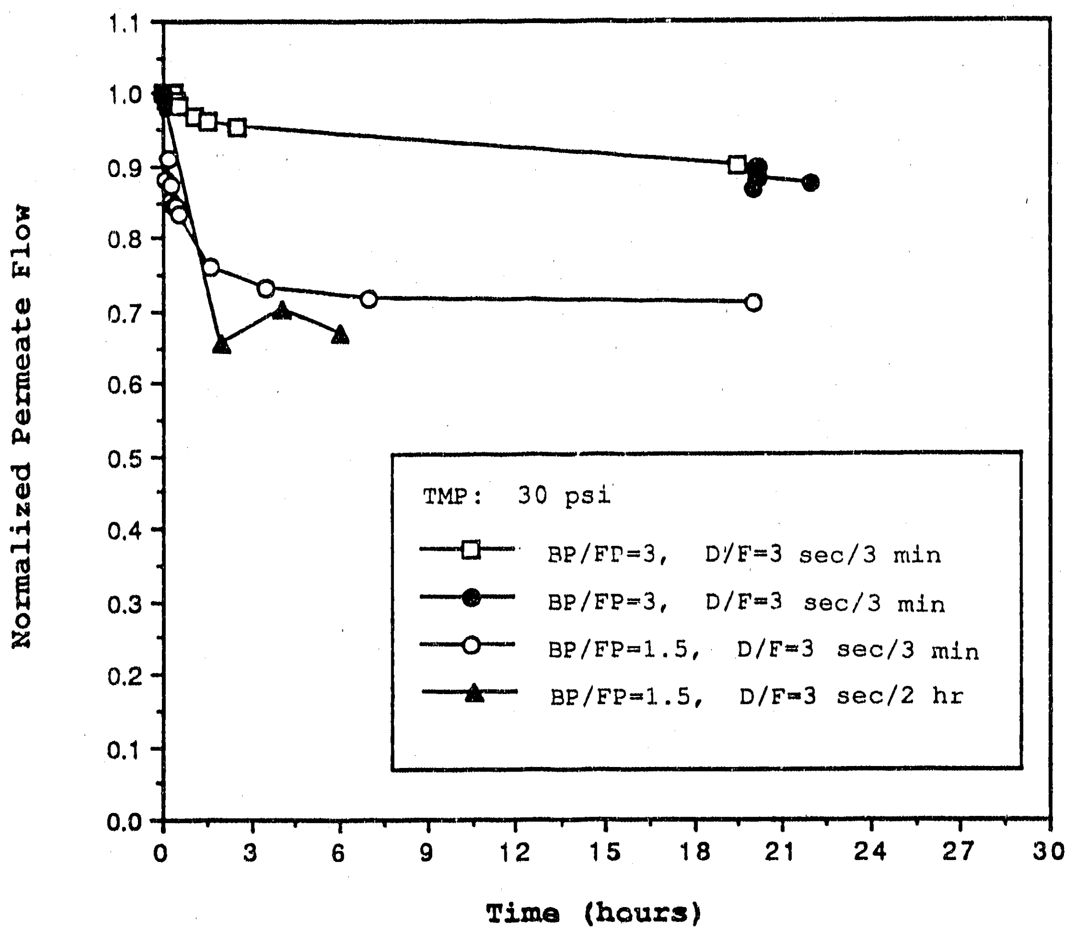

Figure 10. Performance as a Function of Backpulse Parameters

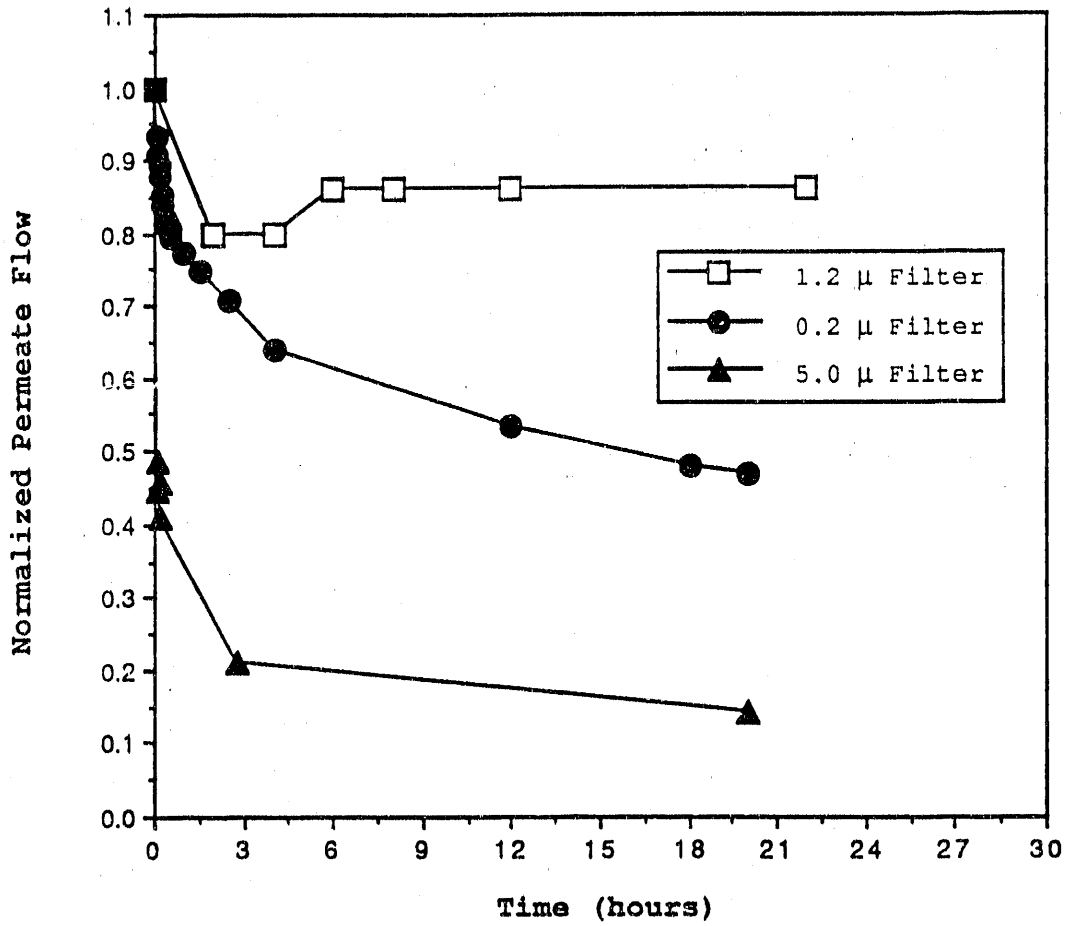

Figure 11. Effect of Pore Size on Filter Performance

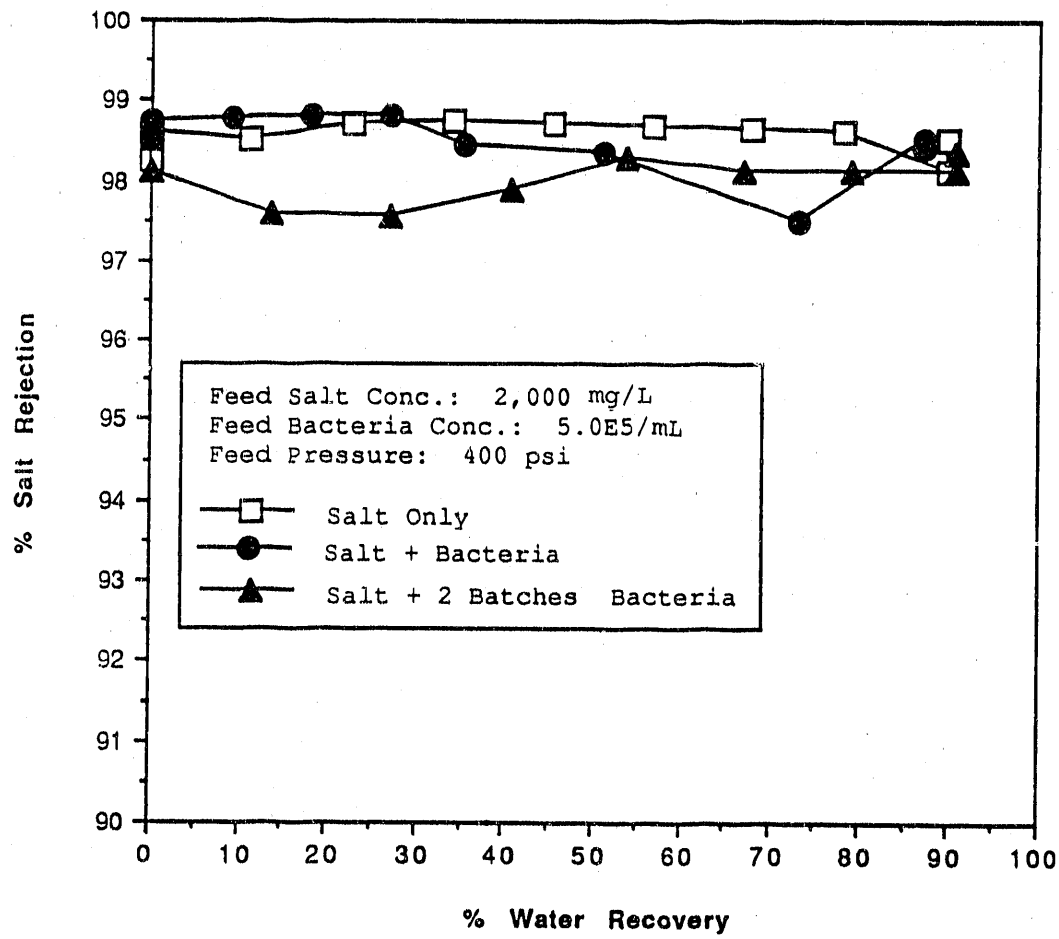

Figure 12. The Influence of Bacteria on Salt Rejection

Table 1. Influent Solute Concentration Range

Nonradioactive Species

Species	Concentration, mg/L min	Concentration, mg/L max
Al	0.0	5.0
Ba	0.0	0.16
Ca	0.39	73.0
Cr	0.0	0.16
Cu	0.0	0.84
Fe	0.0	24.0
Hg	0.0	0.092
K	0.27	1.3
Mg	0.11	1.5
Mn	0.0	0.99
Na	79.0	570.0
Ni	0.0	0.42
Pb	0.0	0.55
U	0.0	1.1
Zn	0.019	82
Cl^-	0.0	130.0
CO_3^{2-}	53.0	150.0
F^-	0.0	8.7
NH_3/NH_4^+	6.9	29.0
NO_2^-	0.0	14.0
NO_3^-	83.0	5300.0
PO_4^{3-}	0.0	81.0
SiO_2	1.3	32.0
SO_4^{2-}	0.0	25.0
TOC	0.3	360.0
TSS	2.0	420.0

Radioactive Species

Species	Concentration, Ci/gal min	Concentration, Ci/gal max
Cr-51	0.0	0.0
Co-58/60	0.0	0.0
Zn-65	0.0	3.7E-9
Sr-89	0.0	0.0
Sr-90	0.0	0.0
Y-90	0.0	0.0
Zr-95	2.0E-8	3.4E-8
Nb-95	1.9E-8	3.2E-8
Ru-103	5.0E-9	7.7E-9
Ru-106	2.1E-8	3.3E-8
I-129/131	0.0	0.0
Cs-134	0.0	1.0E-9
Cs-137	3.1E-8	5.8E-8
Ce-141	0.0	0.0
Ce-144	0.0	0.0
Pr-144	0.0	0.0
Pm-147	0.0	0.0
U-235/238	0.0	0.0
Am-241	0.0	0.0

Table 2. Filtration of Bacteria-Containing Simulants

Simulant	Bacteria/mL	J/Jo(30 min)	J/Jo(final)
DI water	0.9E5	1.0	1.07
DI water	1.0E7	0.57	0.27
Std Inorganic	1.0E5	0.76	0.66
Std Inorganic	1.0E7	0.60	0.29
Std Inorganic	3.0E6[a]	0.76	0.33
Std Inorganic	3.0E6[h]	0.76	0.33
Std Inorganic	1.0E7[c]	0.7	0.43
Std Inorganic	2.0E6[o]	0.80	0.32
Std Inorganic	6.0E6[A]	0.85	0.68

NOTE: a = acid treated, h = heat treated, c = caustic lysed,
o = ozone lysed, A = excess aluminum nitrate added

Table 3. Summary of the Inorganic Fouling Experimental Program

Filter Options Tested	Relative Improvement
Pretreatment Chemistry – Neutralization Reagent	
1. NaOH to pH=7.5 (baseline)	1X
2. NaOH + digestion (40°C)	1.15X
3. NaOH or Na_2CO_3 + high salt levels	1.02X
4. NaOH or Na_2CO_3 + alum	1.05X to 1.15X
5. Rate of NaOH addition	0.75X to 1X
6. Acidify feed, then add NaOH/Carbonate	1.15X to 1.2X/1X
7. Lime or sodium phosphate	1X
8. Na_2CO_3 to pH=7.5	1.15X
Pretreatment Chemistry – Floc Improvements	
1. Polymer flocculants (Betz™) + NaOH	0.4X to 0.5X
2. High Al(III) levels in feed	1.5X to 2X
Mechanical Improvements – Pore Size	
1. NaOH + 0.2 micron filter	1X
2. NaOH + 5 micron filter	0.2X
3. NaOH or Na_2CO_3 + 1.2 micron filter	2X to 4X
Mechanical Improvements – Backpulsing	
1. Low to moderate efficiency backpulsing	0.2X to 1X
2. NaOH + high-efficiency backpulsing	1.2X
Mechanical Improvements – Feed Velocity	
1. Vary (lower to higher) feed velocity	0.5X to 1.2X

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