# 27th ANNUAL WATEREUSE SYMPOSIUM
# CHALLENGES OF HIGH-SULFATE WASTEWATER RECYCLE

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## Abstract

A cement products manufacturer, having a sulfate and total dissolved solid (TDS) limit on its wastewater discharge, is looking for a more environmentally compatible and economically affordable treatment process to replace the barium sulfate precipitation and clarification process currently employed. Water recycling is also a high priority, which is to be part of the system upgrade plan. Engineering study and testing was done to evaluate the process of using Ettringite precipitation followed by tubular microfiltration to remove sulfate and precondition the water for desalination with Reverse Osmosis for reuse within the manufacturing process. The technology evaluation, economic projection, and test protocols and data will be reviewed in the paper.

## Introduction

A US manufacturer of products that are made of cement has a large automated process whereby the molds are filled with cement slurry and the excess liquid is removed by vacuum. The liquid is returned to be mixed into more concrete slurry. Over time contaminants build up in the liquid phase, which if not removed will ultimately degrade the finished product. For this reason a slip-stream of this water is removed and processed for disposal to sewer thus maintaining the levels of the contaminants within tolerable concentrations. The contaminants in question are sulfate and chloride.

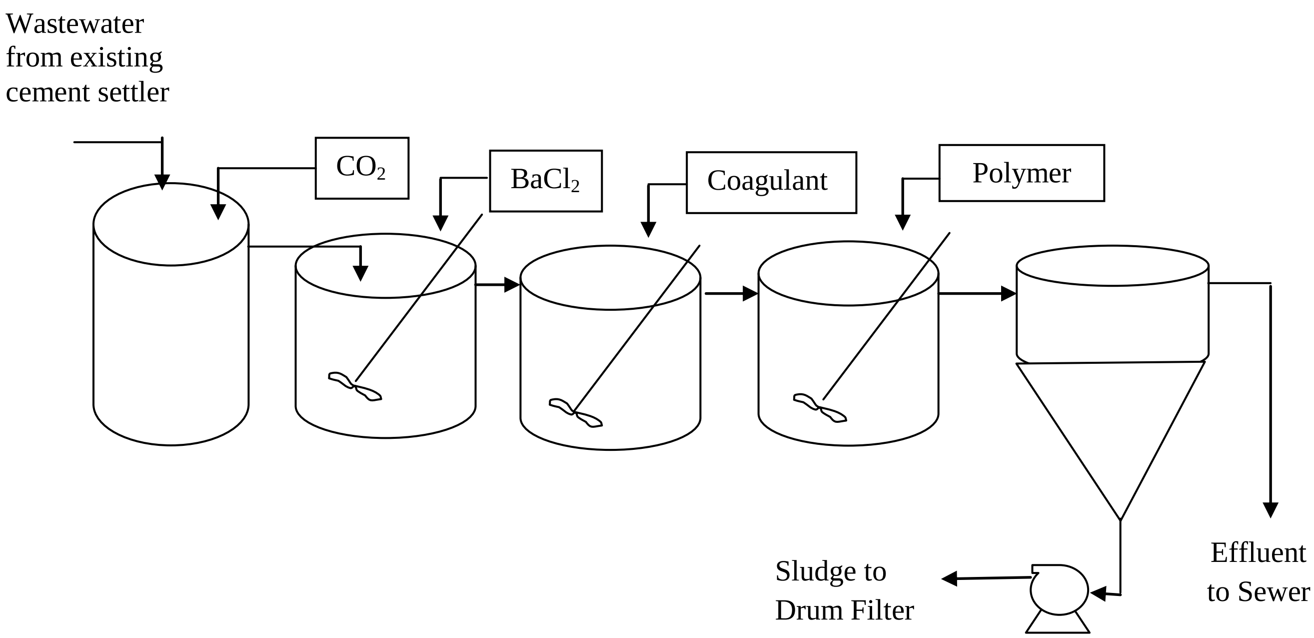
The wastewater plant discharges to a POTW. The POTW has imposed sulfate limitations on the discharge to control crown corrosion within the collection system. The discharge limit is a mass limit of 2,931 lbs. per day or about 1200 ppm based on an average flow of 235,000 gallon per day. They also have a TDS limit of 3,900 ppm. The key contaminants of concern in the influent and the effluent discharge limits are summarized in Table 1.

Table 1 – Influent Contaminants & Effluent Discharge Limits

| Contaminant | Influent | POTW Discharge Limit |
|---|---|---|
| Sulfate | ~2000 ppm | 1,200 ppm |
| Chloride | 80 - 200 ppm | Concern as it adds to TDS |
| TDS | 4048 ppm | 3,900 ppm |
| Calcium | 800 ppm | No Limit but it adds to TDS |
| pH | >12 SU | 9.5 SU |

The current wastewater process, as illustrated in Figure 1, consists of using carbon dioxide $CO_2$ gas to reduce the pH to 8.5. This precipitates some of the calcium as calcium carbonate $CaCO_3$. In the next reaction they add barium chloride $BaCl_2$ to react with the sulfate to make insoluble barium sulfate $BaSO_4$. The solids generated are settled in a clarifier and removed with a rotary drum DE filter. Due to the toxic nature and high expense of the $BaCl_2$ chemical, the plant operators carefully monitor and add just enough chemical to remove sulfate to keep it under their discharge limit. $BaCl_2$ adds a small amount of chloride to the water but the reduction of sulfate and calcium is adequate to keep the TDS in compliance.

Figure 1 – Current Treatment Process Flow Diagram




## Technology Assessment and Planning

To cope with the ever increasing environmental regulations and water scarcity, the company's has established the following water management objectives.

1. Evaluate replacements for the barium chloride with a less expensive and less toxic precipitant.
2. Evaluate water recycle options with an ultimate goal towards Zero Liquid Discharge, if practical.

To achieve the above objectives, the company had initiated an engineering evaluation of various commercially available technologies in the market. A water recycle process utilizing Ettringite sulfate precipitation, tubular microfiltration and reverse osmosis technologies were selected for detailed study based on its successful track record for similar industrial applications.

***Sulfate Reduction Chemistry*** - The sulfate reduction process chosen for further study is Ettringite precipitation. Ettringite is a crystalline material that forms readily when calcium, aluminum and sulfate are present at proper stoichiometric ratios in a high pH condition. The reaction is reliable and can reduce sulfate to very low levels with these benign and inexpensive treatment chemicals. The fact that the reaction occurs at high pH is cost-effective for this application because the wastewater to be treated is already at a pH of over 12 SU.

One drawback to Ettringite precipitation is that the process produces voluminous sludge. The Ettringite solids must be removed prior to the desalination step, such as Reverse Osmosis (RO) filtration, in the water recycle process. For this study, a tubular membrane microfilter was evaluated for its ability to handle a pre-treated stream with high concentration of suspended solids and to produce water with low SDI quality meeting the RO feed specifications.

***Tubular Microfiltration (MF)*** – As show in Figure 2, the microfiltration membranes are manufactured in a tubular configuration capable of handling high solid concentration. The membranes, made of PVDF, are cast on the surface of porous polymeric tubes to produce a nominal pore size of 0.1 micron. The 0.1 micron membrane can provide the fine filtration of UF and the higher flux performance of MF. After chemical reaction, the pre-treated wastewater is processed through the microfiltration membrane filters designed for separation of the precipitates from water. The wastewater is pumped at a high velocity through the membrane modules connected in series. The turbulent flow, parallel to the membrane surface, produces a high-shear scrubbing action which minimizes deposition of solids on the membrane surface. During operation, clear filtrate permeates through the membrane, while the suspended solids retained in the re-circulation loop are periodically purged for further de-watering. An automatic low-pressure back-pulse mechanism is an integral part of the operation design to provide physical surface cleaning by periodically reversing the filtrate flow direction.

Figure 2 – Tubular Microfiltration Modules

Figure 3 – Reverse Osmosis Modules

***Reverse Osmosis*** – The filtrate from the MF membranes is typically pressured between 200 to 600 psig depending on the TDS concentration and processed through thin film composite (TFC) or cellulose acetate (CA) RO membranes (Figure 3). The RO process retains the high molecular weight compounds and allows a small percentage (1 to 3 %) of certain very low molecular weight ions to pass through the membrane. The feed stream is separated into permeate (clean water) usually 75 to 80 % of the feed (recovery) and concentrated brine containing the separated salts (reject). Depending on the percent recovery, the brine may have 4 to 5 times the concentration of salt than the feed water. The permeate will have a TDS of 30 to 150 mg/l, which is less than most city water supply.

## Treatability Study

The object of this treatability study was to:

- Quantify the solids generated in various levels of removal of sulfate
- Determine the best source of aluminum for ease of use and cost
- Determine a treatment protocol that uses the existing equipment as much as possible
- Develop a treatment protocol that is easy to administer and to monitor
- Develop a process for eventual maximum water recycle

***Bench Scale Test*** - The earliest field jar tests were conducted in the customer's facility as simple screening tests to confirm that the sulfate could be removed with the Ettringite crystallization process to very low levels. When the results indicated that it could be removed, further testing was done to learn how to optimize to the objectives listed above.

Two different aluminum salts, Aluminum Chlorhydrate (ACH) and Sodium Aluminate (SOAL), were tested for the Ettringite reaction with selected results presented in Table 2.

Table 2 – Beaker Test Result for ACH and SAOL

| Parameters | Raw Wastewater (Cement Settler Discharge) | ACH Treated Filtrate | SOAL Treated Filtrate |
|---|---|---|---|
| Alkalinity | 2470 | 200 | 3469 |
| Aluminum | 4.57 | 7.4 | 9.85 |
| Barium | 0.181 | 0.119 | 0.154 |
| Calcium | 652 | 183 | 2.91 |
| Magnesium | 0.08 | 0.1 | ND |
| Total Hardness | 1980 | 457 | 7.3 |
| Sodium | 130 | 140 | 860 |
| Iron | ND | ND | ND |
| Manganese | ND | ND | ND |
| Chloride | 102 | 806 | 104 |
| Sulfate | 2257 | 588 | 652 |
| Nitrate | 0.11 | 0.1 | 0.1 |
| Silica | ND | ND | ND |
| Turbidity (NTU) | 1.1 | <1.0 | <1.0 |

| | | | |
|---|---|---|---|
| TDS | 3724 | 2640 | 3724 |
| TSS | 133 | ND | 11 |
| pH | 12.5 | 11.6 | 11.8 |

The bench scale test data demonstrated that SOAL appears to be the better chemistry overall the ACH. It used less lime and aluminum. It also generated less amount of solid while reducing the sulfate by approximately half. Chlorides did not increase, however, sodium did increase. The TDS did remain below the discharge limit. The amount of sludge generated by the process did not appear to pose a problem because it is expected that the sludge would be nonhazardous.

The samples were filtered with 2 micron paper filters instead of microfiltration for these tests and it is expected that the full scale 0.1 micron microfilters will produce lower turbidity as required by the Reverse Osmosis desalination equipment.

***Pilot Testing*** - Based on the promising results of a series of initial bench tests, it was determined to further evaluate the compatibility of the Ettringite chemistry with the MF membrane in a small scale pilot unit.

The pilot test unit consists of a 30-gallon polypropylene tank, a centrifugal re-circulation pump, and two (2) 3-foot membrane tubes with 0.14 $M^2$ (1.5 $ft^2$) membrane area as the major components. A flow meter and pressure gauges are provided for measurement of key operating parameters. All the components are assembled on a SS frame with castors as shown in Figure 4.

A 20 gallon cement settler overflow sample was collected and chemically pre-treated with the Ettringite chemistry. After settling, the supernate solution was collected and treated with carbon dioxide gas for residual hardness and metal precipitation. The precipitated wastewater was placed in the tank and re-circulated by the pump through the membrane modules. The wastewater is pumped at a high velocity through the membrane modules at an inlet pressure of about 25 psig. The turbulent flow, parallel to the membrane surface, produces a high-shear scrubbing action which minimizes deposition of solids on the membrane surface. The concept of the cross-flow microfiltration process is depicted in Figure 5.

Figure 4 – Microfiltration Pilot Test Unit

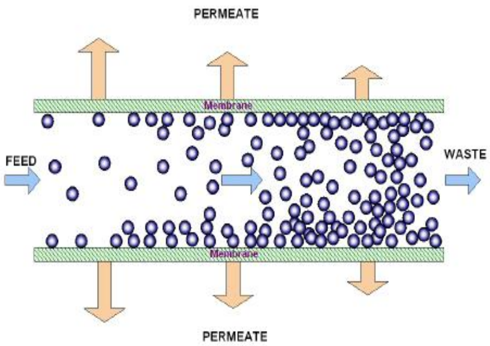



Figure 5 – MF Membrane Solid/Liquid Separation

During the test period, the filtrate flow (flux) was monitored and filtrate samples were collected for analysis. The filtrate flow and analytical data for the key parameters are summarized in Table 3.

Table 3 – Pilot Test Performance & Result Summary

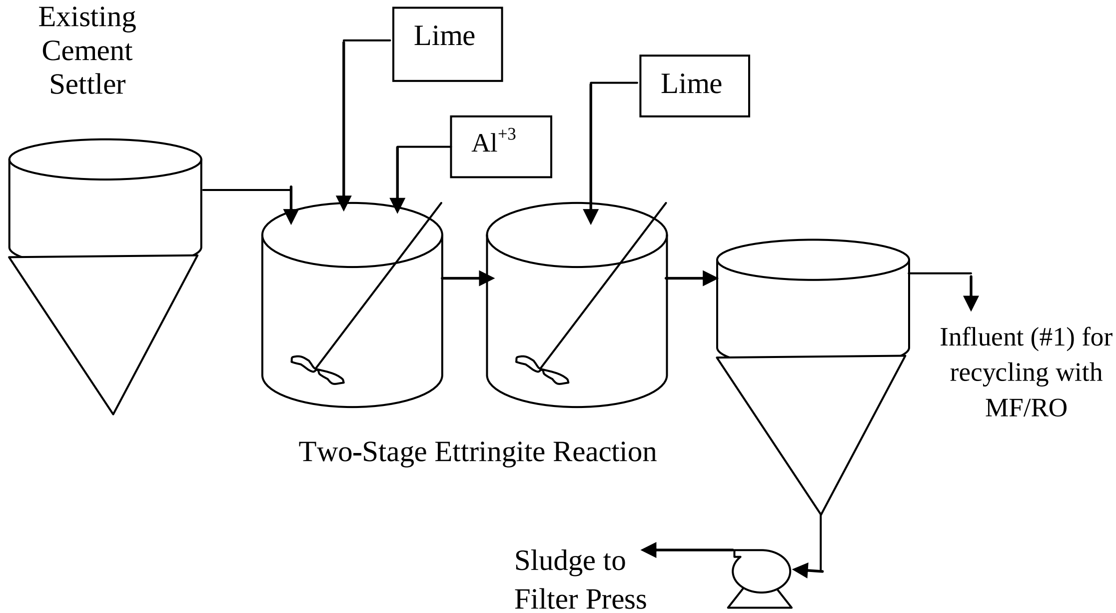
| **Parameters** | **Pilot Test Result** |
|---|---|
| Membrane Flux (GFD) | 300 - 750 |
| Filtrate Analysis<br>Sulfate ($SO_4$)<br>Calcium (Ca)<br>TDS<br>TSS<br>SDI<br>NTU | <br>334 - 650 mg/L<br><5 mg/L<br>2,700 – 3,100 mg/L<br><3.0<br><3.0<br><1.0 |
| Pressure Inlet/Outlet (psi) | 25 / 21 |
| Feed Flow (GPM) | 3 |

The MF filtrate quality is well below the discharge limits for TDS and sulfate and exceeded the quality for the RO feed quality requirements.

## Water Recycle System Design Considerations

As an objective in lowering the equipment capital cost, the existing treatment components were evaluated and re-configured to carry out the Ettringite precipitation process as presented in Figure 6. After a two-stage chemical reaction, the majority of the Ettringite solids are separated by a gravity settler. The overflow from the settler is directed to the microfiltration/RO water recycle system.

Figure 6 – Ettringite Precipitation Process




The sulfate depleted overflow from the settler will receive additional treatment for removal of residual sulfate and hardness by microfiltration before RO desalination. Approximately 88% of the raw wastewater will be recycled from the RO system to production for reuse, while the RO brine solution will be managed by one of the four options illustrated in Figure 7. These options are to be further justified based on the economic values.

## Operating Cost

*Chemical Cost* - SOAL is available as a 45% solution in bulk for approximately $0.50 per pound. The weight per gallon is 12.9 pounds. Based on the consumption used in the test, the total annual cost for the SOAL is projected to be slightly above or the same as the approximately $1,000,000 annual cost for the $BaCl_2$. This may not economically support converting from the $BaCl_2$ without considering the capital costs and a disruption associated with a conversion. However, the non-hazardous Ettringite sludge may outweigh the economic value in the decision making process.

*Other Operating Cost* – Based on the pilot test results and the estimated size of the full-scale system, other key non-chemical operating cost for the MF and RO is summarized in Table 4.

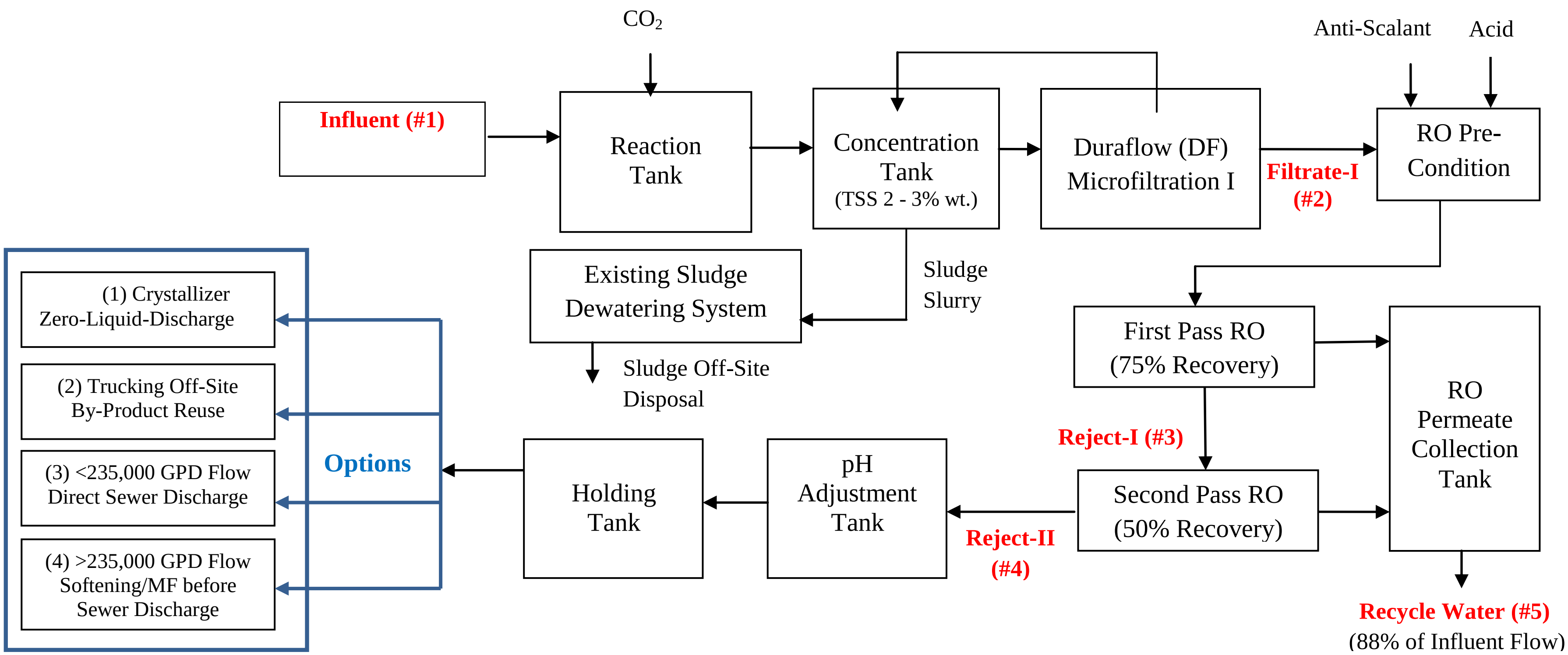
Table 4 – Operating Cost Summary

| Contributors | $USD / 1,000 Gal (Ave) |
|---|---|
| Treatment Chemical | Pre-existing |
| MF Electricity | $0.56 |
| MF Sludge Disposal (Hauling & Land Filling) | Pre-existing |
| MF Membrane Replacement | $0.25 |
| Reverse Osmosis (Chemicals, Electricity & Membrane Replacement) | $2.30 |

## References


1. Cheryan, Munir, Ultrafiltration and Microfiltration Handbook, 2nd edition, CRC Press, Boca Raton, Florida, 1998, pp. 237 – 254.
2. Duraflow, Internal Technical Files, 2005 – 2012.
3. Hydranautics, RO Membrane Foulants and Their Removal from PVD RO Membrane Elements, Technical Service Bulletin, 2009.

## Figure 7 - Proposed Water Recycle Process




| # | Flow Stream from Ettringite | Flow | | SO4 | | Ca (ppm) | TDS (Estimate) | | SDI | NTU |
|---|---|---|---|---|---|---|---|---|---|---|
| | | GPD | GPM | PPM | Lb/Day | | PPM | Lb/Day | | |
| 1 | Influent | 235,000 | 163 | 2,257 | 4,413 | 652 | 3,724 | 7,298 | --- | --- |
| 2 | DF Filtrate I | 235,000 | 163 | 652 | 1,277 | <3 | 3,074 | 6,024 | <3.0 | <1.0 |
| 3 | RO Reject-I | 58750 | 40 | 2,608 | 1,277 | <12 | 12,296 | 6,368 | --- | --- |
| 4 | RO Reject-II | 29,375 | 20 | 5,216 | 1,278 | <24 | 24,592 | 6,024 | --- | --- |
| 5 | Recycle Water | 205,600 | 143 | <20 | --- | <1 | <150 | --- | --- | --- |