

Water Reuse Strategies: Steel Industry Case Studies

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ABSTRACT

Successful reuse of water back into industrial water applications requires a comprehensive understanding of process design, water chemistry, membrane systems, chemical treatment, instrumentation and control. The design of systems and case studies from the steel industry will demonstrate the need for understanding mass balances, process modeling, chemical selection, and membrane applications to operate and recycle water systems reliably and effectively.

Keywords: Reuse, wastewater recycling, reverse osmosis, oily waste, zero liquid discharge.

INTRODUCTION

The steel industry has historically presented challenges for effective water treatment because it is a high water user and the applications may involve high heat, critical non-contact cooling, direct contact cooling, high suspended solids waters, oil and grease contamination, and complicated cascading.

The first step in treating the cooling waters used in a steel mill or steel processing plant is to thoroughly understand the water characteristics, systems, contaminants loading, treatment systems used and their effectiveness, retention times, and water quality requirements. A mass balance around the water and the constituents helps to determine needs and opportunities.

A common goal is to reuse as much water as possible within the various water systems and work toward minimal discharge or zero liquid discharge. Crown and Veolia have been involved in many efforts to reach this goal and both mechanical and chemical strategies are typically needed to handle the stressed conditions created.

A. RECYCLE OF PLANT EFFLUENT

Crown evaluated the wastewater treatment process for a steel processing plant where we modified the existing wastewater treatment chemistry and then installed and operated a side-stream pilot plant to determine the chemical and equipment strategy necessary to reuse the wastewater with an enhanced physical/chemical treatment as a pretreatment to reverse osmosis (RO).

In Phase I of the study, analytical data was gathered to determine influent and effluent characteristics of the present treatment program (see Figure 1 and Table 1). Some chemical treatment adjustments and changes were made, and further laboratory analyses were performed.

In Phase II, a side-stream flow of the treated wastewater was taken through an equipment pilot plant. This pilot consisted of a continuously backwashing sand filter, activated carbon filtration, multi-media filtration, sodium zeolite water softener, and an RO machine. The capacity of the equipment pilot plant was approximately 5 gallons per minute (GPM).

Phase III included a full-stream implementation plan and cost evaluation.

Objectives

The objectives of the plant management team were to determine a strategy that would reduce the plant's wastewater discharge rate to meet a new quantitative discharge limit, meet the constituent discharge limits of the POTW, successfully reuse the treated wastewater back into the plant, and improve plant economics. The primary reuse points would be cooling tower makeup and ion exchange demineralizer supply where the demineralized water is used for the cleaning of the steel coils prior to zinc coating (see Figure 2).

The wastewater treatment plant collects wastewater in two 150,000-gallon equalization tanks. The cleaners, oils, and rinse waters from the process lines, along with cooling tower blowdown and other wastewaters, mix prior to the physical/chemical treatment process of coagulation, flocculation, gravity separation, and filtration.

Figure 1: Initial Plant Water Balance

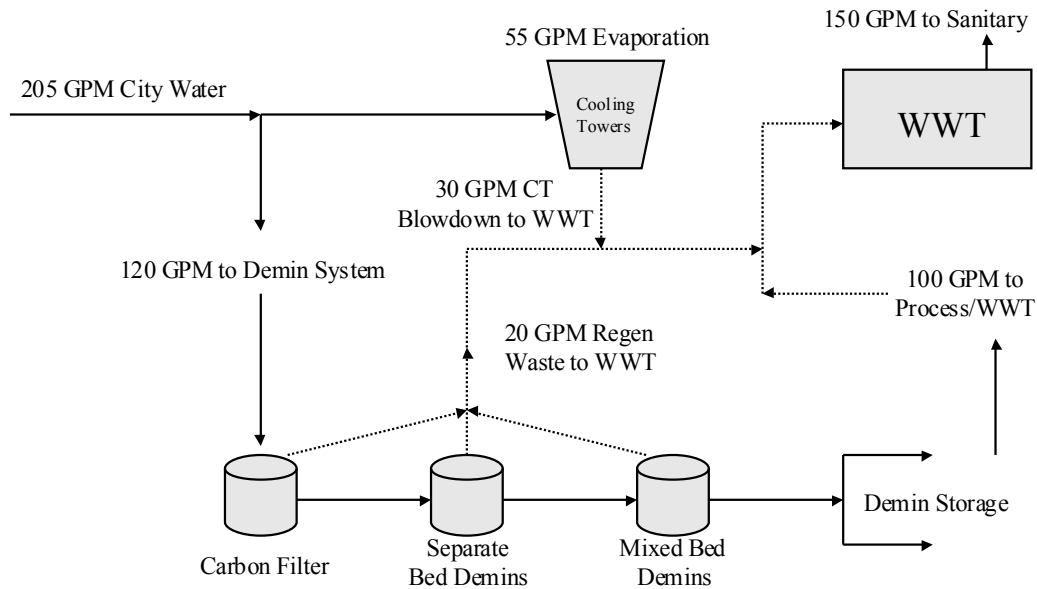


Table 1: Water Characteristics

	City	Treated Wastewater
Conductivity	650 μ S	5300 μ S
Total Hardness mg/L as CaCO ₃	200	220
Calcium mg/L as CaCO ₃	88	100
Total Alkalinity mg/L as CaCO ₃	35	230
Chloride mg/L as Cl	80	320
Sulfate mg/L as SO ₄	180	680
Silica mg/L as SiO ₂	6.5	9.6
Iron mg/L as Fe	<0.05	1.0
Strontium mg/L as Sr	3.5	9.8
Barium mg/L as Ba	<0.05	<0.05
Aluminum mg/L as Al	0.20	0.6
pH S.U.	8.0	8.5
Oil and Grease mg/L	ND	14
SDI	5.0	Not achievable

Constituents of concern for recycling to the RO and back into the plant included:

- Oil and Grease
- Total Suspended Solids
- Microbiological
- Surfactants
- Iron
- Strontium
- Aluminum
- Zinc
- Chlorides
- Sulfates

Chemical Removal Strategies

1. **Oil and Grease:** Apply ferric chloride or ferric sulfate and an organic coagulant along with bentonite clay to the reactor tank. Increase and maintain heavy solids level in the reactor tank.
2. **TSS:** Recycle solids to reactor tank. Find the most effective flocculant.
3. **Microbiological:** Sodium hypochlorite.
4. **Surfactants:** Coagulants, bentonite clay.
5. **Iron:** Replace ferrous chloride with ferric chloride. This eliminated the need for air to the reactor tank and avoided the possibility of incomplete oxidation of ferrous to ferric.
6. **Aluminum:** Coagulants and pH adjustment.
7. **Zinc:** pH adjustment.

Mechanical Strategies

1. **Oil and Grease:** Continuously backwashing sand filter and activated carbon filter.
2. **TSS:** Continuously backwashing sand filter and multimedia filters.
3. **Microbiological:** Ultraviolet radiation (UV).
4. **Surfactants:** Activated carbon filter.
5. **Iron:** Continuously backwashing sand filter, multimedia filters, and sodium zeolite softeners.
6. **Strontium:** Sodium zeolite softeners.
7. **Aluminum:** Sodium zeolite softeners.
8. **Zinc:** Continuously backwashing sand filter and multimedia filters.
9. **Anions:** RO.

An RO antifoulant was recommended to help disperse any remaining contaminants. The chemistry of an antifoulant usually consists of phosphonates or organic polymers. The selection of the chemistry is dependent upon the residual contaminants in the feedwater to the RO. Proper selection of the antifoulant can significantly increase the allowable contaminant loading and head off scaling and fouling. Care must be taken in selecting the chemistry to prevent an antagonistic effect between contaminants and the antifoulant.

Equipment Strategy

A continuous backwashing sand filter was recommended after the Inclined Plate Clarifiers (IPC) to remove most of the suspended solids. Pilot testing suggested that the sand filter should be followed by a pressure filter containing multimedia with an activated carbon cap. This filter and carbon would remove remaining suspended solids and organics remaining after the fluidized bed sand filter, and provide additional insurance against upset conditions.

The use of softeners after the multimedia filter removes remaining hardness ions, iron, aluminum, and strontium. All of these are potential foulants for RO membranes. This strategy also showed a reduction in SDI and allowed the water to potentially be used in other areas, such as the cooling tower, in the future.

Because of the high microbiological slime problem observed, the use of UV lights was recommended as a sterilant in addition to the chlorine. UV lights would require relatively low maintenance. The light bulbs require replacement approximately once a year.

Recycling wastewater to an RO machine requires very consistent pretreatment, and therefore should offer some redundancy in the pretreatment strategy. The pretreatment equipment that was recommended offers that redundancy. See Figures 3a, 3b, and 3c for the modified wastewater flow diagrams.

Automation and Operation

Because there is variability in the waste stream, and the inherent nature of wastewater treatment involves upset conditions, automation should be utilized as much as possible, but close operator attention would be required.

The ferric chloride and polymer continued to be fed automatically based upon influent wastewater flow. The clay feed system and the flocculant would also be linked to influent flow to automatically adjust feedrates.

Hypochlorite can be controlled with ORP, a chlorine analyzer, or initially the pump could be pulsed based upon wastewater flow.

Turbidity meters were recommended to monitor for upset conditions from the ICP and/or sand filter. Softeners would regenerate automatically based upon flow, and the multimedia filters will backwash based upon differential pressures.

Full-time operator attention was anticipated for the wastewater treatment, wastewater recycle, and demineralization area. Regular visual inspection of all the equipment and the water itself is required so that immediate action can be taken with upsets or equipment problems. Failure to react immediately can lead to RO membrane fouling and shutdowns.

Cooling Water Chemistry

The RO effluent would become the primary water source to the cooling tower and other plant processes along with some city water. The water would have possible residual low molecular weight organics, and the inorganic content would vary based upon plant loads, operation of the wastewater treatment plant, and operation of the RO. The strategy is to run high cycles of concentrations in the cooling towers at 12-15 to minimize discharge to waste. The concern for scale, corrosion, and microbiological activity at the high cycles and variable conditions required the use of high performance chemistry.

Because the cooling water chemistry can change from a very low hardness and corrosive water to a high hardness scaling water where the Langeliers Saturation Index (LSI) approaches 3.0, the inhibitor program utilizes phosphate, zinc, and azole as corrosion inhibitors along with a phosphonate blend incorporating PBTC. Key to the program is a blend of polymers including a high performance sulfonated polymeric dispersant that inhibits and disperses calcium carbonate at the high LSI's.

The alkalinity of the makeup can also vary dramatically, so the biological treatment includes sodium hypochlorite addition controlled by ORP along with the feed of sodium bromide that creates hypobromous acid when used with the sodium hypochlorite.

The treatment provides clean cooling systems with mild steel corrosion rates consistently below 1 mil per year.

Figure 2: Process Water Flow Diagram

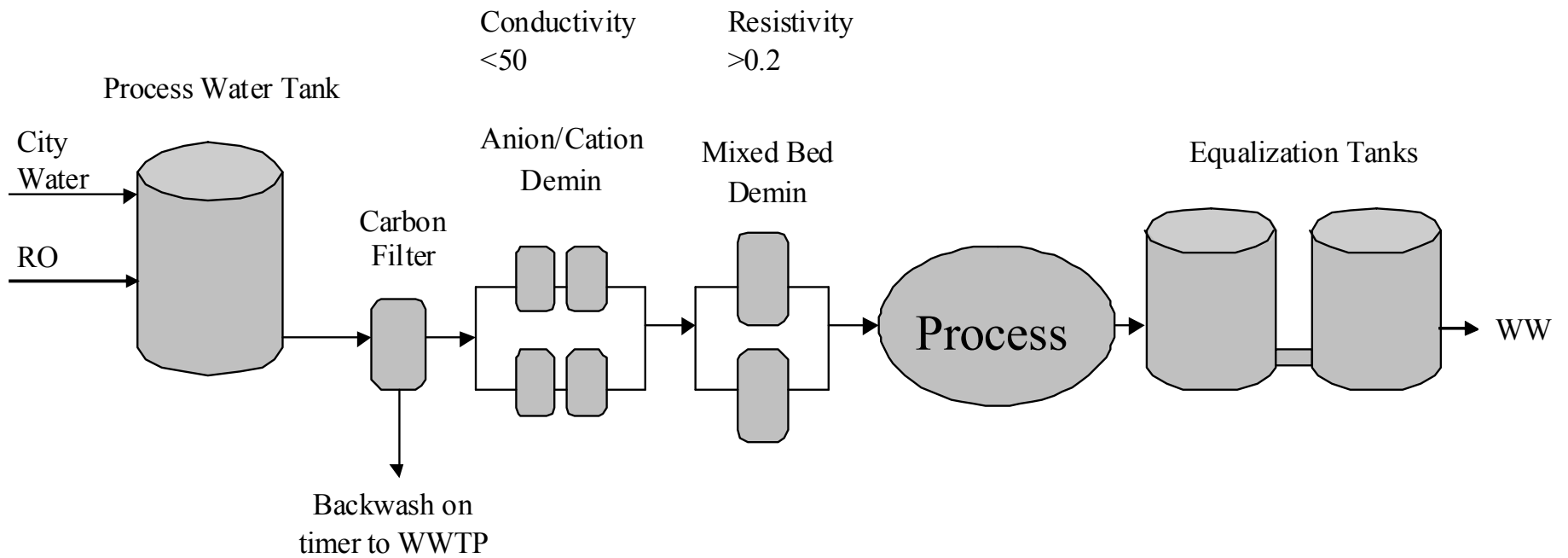


Figure 3-a: Wastewater Flow Diagram

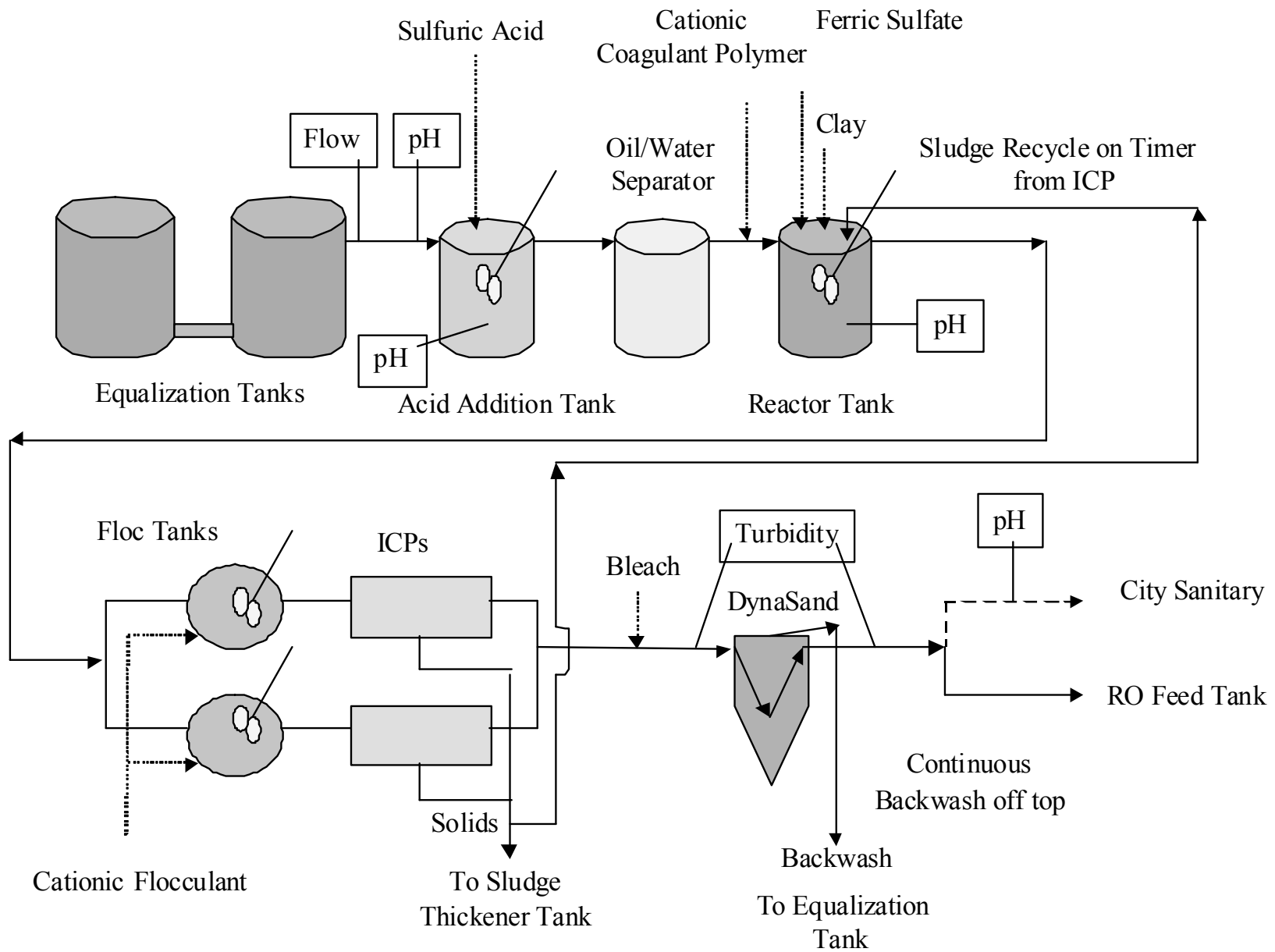


Figure 3-b: Wastewater RO Flow Diagram

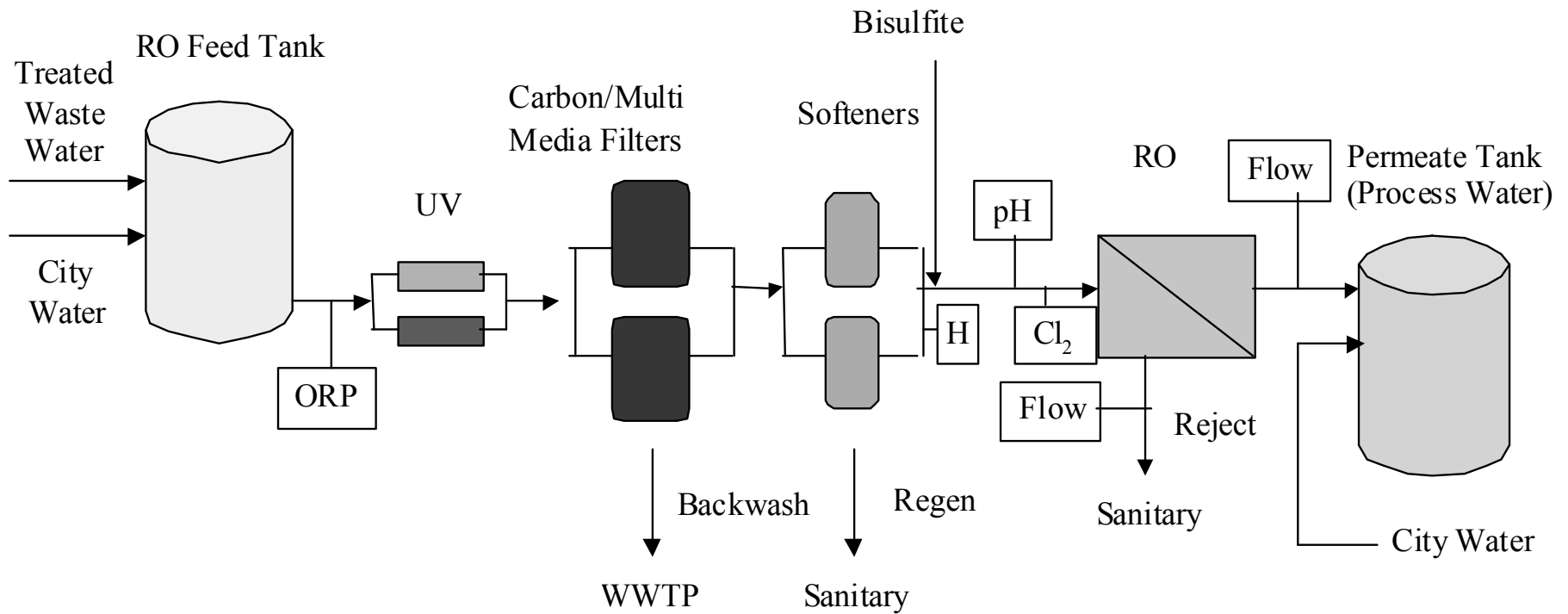
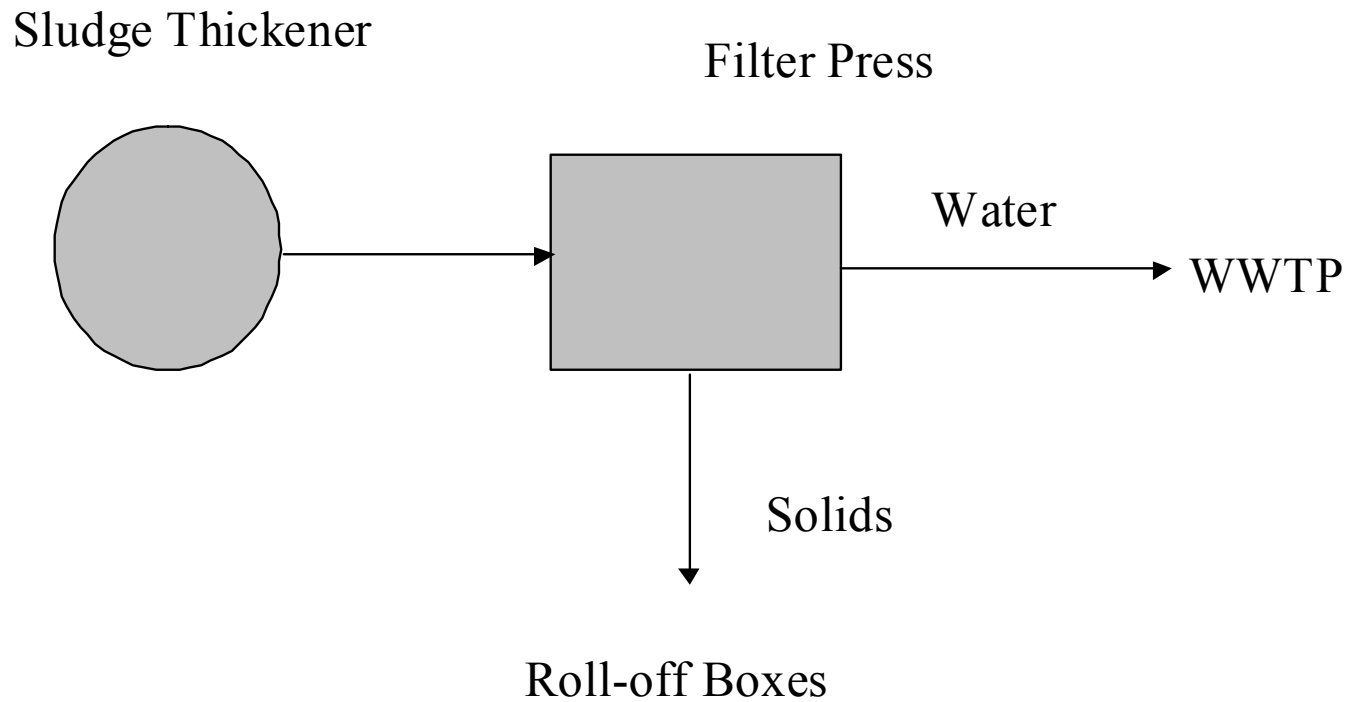


Figure 3-c: Wastewater Sludge Handling Diagram



B. STEEL MILL CONTACT WATER TREATMENT

In the steel manufacturing process where the molten steel is cast, high volumes of water are used to quench and cool the steel. This contact or direct cooling water becomes contaminated with high levels of suspended solids and mill scale along with oil and grease. Because of the quantity of water required, it is necessary to cool this water and reuse it.

Scale pits are used to provide retention time and a place to settle out solids and perhaps remove some oils with skimmers. Also clarifiers and media filters may be used to help clean this water before it is cooled, commonly over cooling towers, and then reused.

It is often necessary to apply coagulants and flocculant to chemically assist the removal of the solids and oils. The chemistry used to accomplish this can conflict with chemicals applied for corrosion and deposition control. This antagonistic effect between contaminant removal and contaminant stabilization requires careful consideration, control, and monitoring.

Commonly, ferric chloride and/or aluminum products such as alum are used as part of the coagulation program in contact waters. They are applied to coagulant oils and colloidal particles for separation and removal from the recirculating water to help maintain tolerable suspended solids and oil concentrations. Unfortunately, both aluminum and iron salts are very effective at precipitating orthophosphate which is a primary corrosion inhibitor used in the cooling waters. The net result of using ferric or alum and phosphate together is that they consume each other and create suspended solids and higher dosage requirements. Iron and aluminum are also known to consume and deactivate polymeric dispersants that are necessary to stabilize phosphate, zinc, and phosphonate treatment chemistry and to disperse suspended solids.

One way to effectively address this conflicting chemistry is to avoid as much of it as possible in the first place. Organic coagulants can be considered instead of aluminum or iron based products. These products include the EPIDMA's, polyDADMAC's, tannins, and starches. The high cationic charge of these organic chemistries can, however, also have antagonistic effects. Anionic organic dispersants can react with them creating a precipitant and potential organic foulant. Reaction of particularly the EPIDMA and DADMAC has been reported in studies by Amjad and Zuhl.

If aluminum or iron based coagulants cannot be avoided, then it is our experience that it is best to apply high performance polymeric dispersants and at dosages that can still effectively perform their designed functions.

If organic coagulants are used, then testing with the polymeric dispersants is advisable to see what kind of interaction they may have and how performance of each are affected.

Feed location can become very important, especially when there is some interaction of the coagulants, inhibitors, and dispersants. For example, in a scale pit the coagulant and

flocculant should be applied upstream and removed as much as possible in the scale pit or side-stream system, and the inhibitor and dispersant replenished on the effluent from the scale pit on the way to process cooling.

C. ACHIEVING MINIMAL DISCHARGE OR ZERO LIQUID DISCHARGE

With the goal or necessity of minimizing water consumption and plant discharge, the water balance of steel mills and steel processing plants must be well understood and managed to avoid adverse effects of the minerals present in the makeup water and contaminants that enter during processing and cooling.

In a tight integrated plant it is good to determine the overall water balance and the plant cycles of concentration at each location based upon makeup flows, evaporation, and water losses. The ionic or mineral balance should also be determined. It is useful to have the plant balance tied together in a spreadsheet so that any changes made or considered are modeled by the spreadsheet.

High amounts of water evaporation occur from the cooling towers and the direct cooling applications. Depending on the process, some minerals are removed as drag out in the direct cooling. Most minerals should remain in the water from cooling tower evaporation. Some can be lost to cooling tower drift and windage. In damaged cooling towers, the drift can sometimes be significant.

As part of the treatment strategy and control, it is necessary to know the removal efficiency of solids and oil and grease in and out of scale pits or side-stream treatment processes such as deep bed filters or clarifiers. This will help control coagulant and flocculant dosages and determine dispersant chemistry requirements and dosages.

Control of bacteria, fungus, and algae can be a challenge because of organic loading on many of the waters, along with high volumes and warm water temperatures. The large system volumes and high contaminant loading can create high chemical costs, especially for nonoxidizing biocides that require a relatively long retention time and high dosages to be effective.

Sodium hypochlorite can be effective and relatively inexpensive as the primary biocide, often times even at high pH. Sometimes it may be advantageous to supplement the chlorine source with sodium bromide in high pH waters such as 8 – 9.4. Chlorine dioxide can also be a good choice for the contaminated and highly stressed conditions of some steel mill waters.

In a cooling system, for corrosion inhibitors to react properly with the metal and form a corrosion barrier, the surface needs to be clean and free of biofilm, suspended solids, or scale, so the use of biodegradants can be very helpful.

Biodetergents (Also called: Biodispersants or Biopenetrants or Organic Dispersants)

Chemicals that can penetrate and loosen the complex matrix of biofilms allow biocides to reach the organisms for more effective kill and control. These chemicals are typically shot fed at dosages that break down polysaccharides, emulsify oils, release minerals and foulants, or disperse the biopolymers. Sometimes they are fed continuously.

The biofilms are often the glue that allows suspended solids found in recirculating water to be bound to the surface of the cooling system components including heat exchangers, piping, and the cooling tower structure. Mineral deposits are also commonly found within this matrix. Calcium and magnesium offer bridging mechanisms to strengthen the polysaccharide polymer chains. Corrosion occurs underneath the biofilms, releasing corrosion byproducts that become part of the matrix also.

Because accumulations of dirt and the formation of biofilms can lead to corrosion and scaling, their prevention through the use of filtration, biocides, and biodetergents can be extremely important for a successful water management program.

Biodetergents help keep cooling systems clean or help clean up fouled systems by dispersing the extracellular material created by bacteria, algae, and fungus. They help biocides to penetrate and kill the biological growth. By keeping the surfaces clean, they allow scale and corrosion inhibitors to perform better.

Some biodetergents can create foaming conditions especially at high dosages, so care must be taken in product selection and applying the product. Also, the compatibility with other treatment chemistry, especially oxidizing biocides, should be considered.

Some biodetergents include:

- ◆ DTEA II (2-Decylthio ethanamine)
- ◆ DMAD (Fatty acid amide)
- ◆ Dodecylamine acetate
- ◆ Polyquaternary amines
- ◆ DOSS (Dioctylsulfosuccinate)
- ◆ Polyoxyalkylenes
- ◆ Enzymes

Control of corrosion and deposition in high stress waters

In zero liquid discharge or minimal discharge systems a comprehensive understanding of the constituents in the water and the range of the constituents is very important since they can change based upon operational factors, makeup water chemistry, and control.

Corrosion control: Orthophosphate, polyphosphates such as tetrapotassium pyrophosphate, zinc, phosphonates, polysilicates, molybdate, azoles, and others can be

used to reach effective corrosion protection. The dosage requirement and combination depends upon the specific water and application. Stabilization of the phosphates and phosphonates will often time require high performance polymers.

Deposition control: When the cooling waters become highly stressed or variable because of water reuse and recycle, more consideration must be given to polymeric dispersant selection and phosphonate selection.

If high levels of oxidant are necessary for biological control, the use of the phosphonate 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) becomes a good choice since it has high resistance to oxidation. Also if high cycles create high calcium levels, the PBTC is a good choice since it has high calcium tolerance before it precipitates with the calcium.

Crown has steel experience where the makeup water silica concentration has been greater than 60 mg/L as SiO₂ in a zero liquid discharge plant. Treatment technology has been applied to lower that number, but still very high levels of silica can and have occurred with water recycling and high cycles. Silica specific polymeric dispersants and phosphonates can be applied that can allow high levels of silica to be reached in the systems without deposition. It is our experience that the silica levels that can be attained are specific to each water and location. Silica chemistry is complex and its stabilization is also greatly influenced by the other constituents in the water, scale control of those other constituents, temperature, and pH.

Selection of polymers that can provide for stabilization of phosphates, phosphonates, iron, and zinc become critical in highly stressed waters seen in steel processing plants where the water is reused and recycled. Depending upon the constituents in the water, it may be advantageous to apply a combination of polymers including high performance sulfonated polymers. The polymers may have to handle high LSI conditions, perform in the presence of deactivators such as aluminum or iron, be able to stabilize phosphate at high calcium and/or high pH conditions, and disperse high levels of suspended solids.

CONCLUSIONS

Having a comprehensive understanding of the mass balance of water and the constituents in water is a first step for water reuse in a complicated industrial plant such as steel manufacturing or processing. The contaminants and the chemistries applied can have significant interaction so they should be carefully selected and evaluated for each particular situation.

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