Technical Paper

Industrial Water Reuse and Wastewater Minimization

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Abstract

Many industrial users of fresh water are under increasing pressure to reuse water within their facilities. Their goal is to minimize the amount of water that is discharged, either to a receiving stream or a publicly-owned treatment works. There are a variety of reasons for this pressure, such as:

- The cost of fresh water (US$1.00 to US$2.00/1,000 gal or US$0.26 to US$0.52/m^3)
- The cost of additional treatment to reach discharge limits (US$2.00 to US$4.00/1,000 gal or US$0.52 to US$1.04/m^3)
- Water availability
- Environmental awareness
- Community relations

This paper will address some of the reuse techniques available to industrial users and detail the results of these techniques.

Reuse of Refinery Wastewater as Cooling Tower Makeup

In many refineries, makeup water to the cooling tower can account for up to 50% of the total demand for fresh water. A water balance for a 125,000 bbl/day Gulf Coast refinery is shown in Figure 1.

At this refinery, the makeup demand of the cooling tower is almost 60% of the total water demand. City water, at a purchase cost of US$1.40/1,000 gal ($0.36/m^3), is the makeup water source. The dissolved solids concentration of this water is highly variable as shown in Table 1.

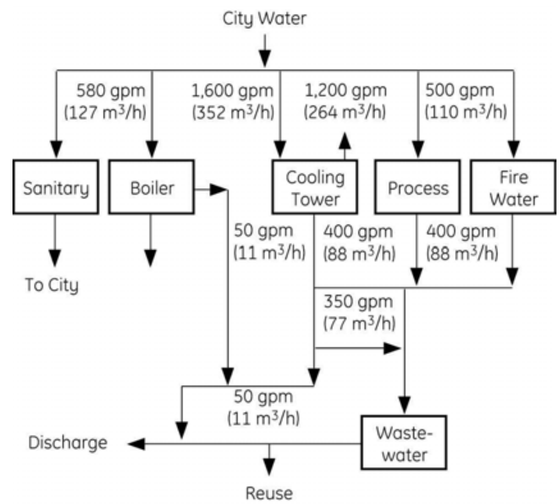

Figure 1: Refinery water balance

Table 1: Raw water analysis

Parameter	Concentration
Specific Conductance	530-850 μmhos
Ca^{+2}	115-180 ppm (mg/L)
Mg^{+2}	25-45 ppm (mg/L)
Na^{+}	40-90 ppm (mg/L)
Cl^{-}	70-135 ppm (mg/L)
$SO4^{-2}$	45-70 ppm (mg/L)
$PO4^{-3}$	0.2-0.4 ppm (mg/L)
SiO_2	13-18 ppm (mg/L)
Alkalinity	118 ppm (mg/L)
pH	8.4

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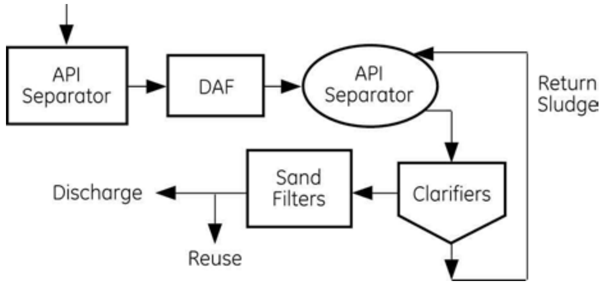

Figure 2: Refinery waste treatment plant flow diagram

Table 2: Wastewater analysis

Parameter	Concentration
Specific Conductance	4,500µmhos
Ca+2	190 ppm (mg/L)
Mg+2	120 ppm (mg/L)
Na+	830 ppm (mg/L)
Cl-	700 ppm (mg/L)
SO4-2	1,120 ppm (mg/L)
SiO2	21 ppm (mg/L)
Alkalinity	272 ppm (mg/L)
COD	20-40 ppm (mg/L)
PO4-3	8-10 ppm (mg/L)
pH	8.3 ppm (mg/L)

Due to a number of factors, including the cost of fresh water and its availability, water reuse of the waste treatment plant effluent was evaluated. The waste treatment plant flow diagram is given in Figure 2. A typical wastewater analysis is given in Table 2. A number of water conservation measures, such as cascading cooling tower blowdown, had already been employed.

Reuse of the wastewater as cooling tower makeup was begun, with reuse water comprising up to 20% to 50% of the makeup requirements. Table 3 shows the water chemistry for the crude unit tower with and without the use of recycle water.

As would be expected, reuse of the high conductivity wastewater as makeup led to an increase in conductivity in the cooling tower recirculating water, resulting in a more aggressive supply water to the various heat exchangers in the refinery. Most of the heat exchangers are constructed with mild steel tube sheets and bundles, although the surface condensers present in the plant contain admiralty tube bundles.

The cooling water chemical treatment program administered to provide corrosion protection is given in Table 4. The polymer used in this treatment program is an acrylic acid/allyl hydroxyl propyl sulfonate ether copolymer. Corrosion results, as measured by 90-day corrosion coupons, are generally <1.0 to 1.5 mpy (<0.03 to 0.04 mm/y) on mild steel and 0.1 to 0.2 mpy (0.003 to 0.005 mm/y) on admiralty.

One of the biggest concerns when reusing wastewater at this refinery, and at others that are reusing wastewater, is the variability of the makeup source. This is compounded at this refinery because the city water makeup is also highly variable as seen in Figure 3.

Calcium levels are of particular concern because the blowdown rate from the towers is based on

Table 3: Cooling tower water analysis

Parameters	City Makeup Water	City and Wastewate Makeup Water
pH	7.3	7.3
Conductivity	3,200µmhos	9,090µmhos
Ca^{+2}	680 ppm (mg/L)	710 ppm (mg/L)
Mg^{+2}	160 ppm (mg/L)	300 ppm (mg/L)
Na^{+}	360 ppm (mg/L)	1,420 ppm (mg/L)
Cl^{-}	520 ppm (mg/L)	1,840 ppm (mg/L)
$SO4^{-2}$	280 ppm (mg/L)	2,080 ppm (mg/L)
Alkalinity	70 ppm (mg/L)	70 ppm (mg/L)
SiO_2	72 ppm (mg/L)	95 ppm (mg/L)
$PO4^{-3}$	10-12 ppm (mg/L)	15-18 ppm (mg/L)

Table 4: Chemical treatment program

Parameter	Concentration Range
Orthophosphate	10-12 ppm (mg/L)
Pyrophosphate	1-2 ppm (mg/L)
Copolymer	10-12 ppm (mg/L)
Zn^{+2}	1-2 ppm (mg/L)
Azole	1-2 ppm (mg/L))
pH	7.2-7.4
Free Chlorine Residual	0.2-0.4 ppm (mg/L)

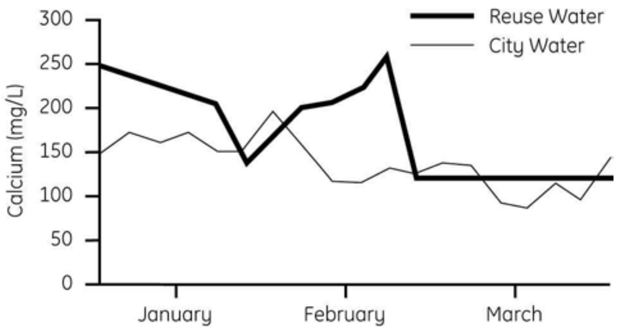

Figure 3: Variability in calcium concentration

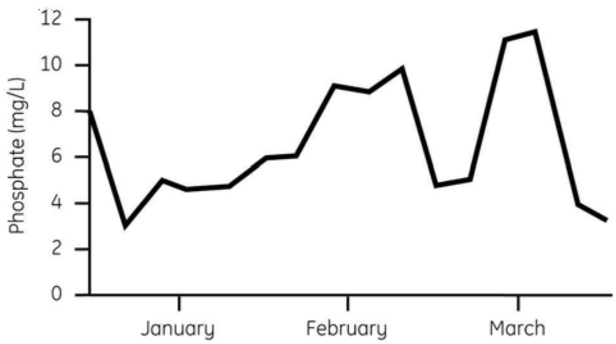

Figure 4: Variability in phosphate concentration over time

calcium levels and calcium sulfate concentration. Calcium levels are maintained at <1,100 ppm (mg/L) and the calcium sulfate product is maintained at <5 × 106 ppm (mg/L). Historically, most of the cooling towers have run at approximately six cycles of concentration when employing the reuse water as partial makeup.

Figure 4 shows the variability in phosphate concentration, which also is important in balancing the overall water chemistry in the towers. Due to this variability, monitoring and control of the cooling system is critical.

Some of the lessons learned from reusing a highly variable water source as cooling tower makeup are as follows:

- Purge High Salt Content Streams - Figure 1 shows that the blowdown from the boiler house, as well as some of the cooling tower blowdown, bypasses the waste treatment operation. Since the soluble salts present in these streams are relatively untouched by the unit operations present in most refinery waste treatment plants, bypassing does not decrease contaminant removal efficiency. By blending these streams after the takeoff point for the reuse water, salts can be purged from the system so that additional water can be reused.
- pH Control - Redundant pH control is employed at all ten cooling towers at this refinery. Because of the availability of water, water reuse is maximized. This means pushing the water chemistry, particularly the calcium levels, as far as possible. Redundant pH control allows this to be accomplished without the fear of heat exchanger scaling.
- Water Balance - It is important to keep the city water to reuse water ratio as constant as possible. For example, when the heat load changes, one makeup source should not provide all the water, while the other source is shut off completely. The ratio of each should be constant as the flow rate changes.
- Monitoring and Control - The ability to reuse wastewater effectively is directly related to the ability to adjust to changes and keep the system in control. Daily tests are run on each of the towers, so that with information supplied by the wastewater operations personnel, daily decisions on chemical feedrates, blowdown rates, etc., can be made.
- Upsets - It is a fact of life that upsets to the waste treatment plant will occur, just as leaks occur in cooling water systems. Gaseous chlorine is used for microbiological control at this site. The contaminants that will affect microbiological control include ammonia, phenol, and sulfides. During upsets, corrosion rates will increase to 10 to 15 mpy (0.25 to 0.38 mm/y), but corrective action can minimize the long-term impact.

Reuse of secondary treated water is effectively accomplished at this refinery by employing all of the above techniques.

Reuse of Demineralizer Rinse Waters

Demineralizers are found in many industrial operations for the production of high quality water for use as boiler feedwater and other process uses. The regeneration of demineralizers is usually accomplished in four steps: backwash, acid/caustic introduction, slow rinse, and fast rinse.

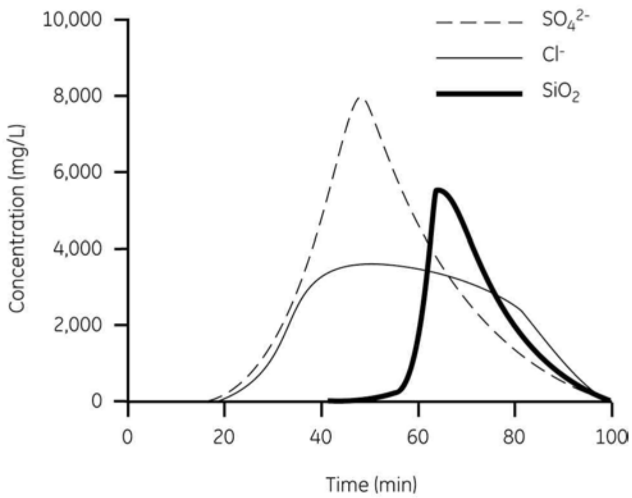

Figure 5: Demineralizer regeneration rinse water

A major southwestern chemical complex was having problems with effluent toxicity. One of the aggravating parameters was the total dissolved solids concentration of their wastewater, which approached 5,000 μmhos. At least 25% of the salt concentration was due to regeneration of the demineralizers. This plant uses a low alkalinity water for makeup to their cooling towers. Sodium hydroxide is added to maintain a recirculated water pH of 8.2 to 8.4.

Reuse of demineralizer rinse waters had three purposes:

- Sodium hydroxide reduction
- Water conservation
- Effluent toxicity reduction

Other reuse schemes using demineralizer rinse waters combine the cation and anion rinse waters to provide a neutral pH stream that can be used as cooling tower makeup. This particular case was unique in that sodium hydroxide was used for cooling tower pH adjustment and acid was used on the waste stream before treatment due to the stream's alkaline nature. Removing a source of alkalinity (in this case anion rinse waters) allowed a reduction in acid usage. This had a positive impact on the salinity of the wastewater.

A program was instituted to evaluate the possibility of reusing the regenerant waste as cooling tower makeup, both for the sodium hydroxide value and as a water reuse measure. Carbon dioxide was already used to neutralize the combined plant waste waters before biological treatment. Removing an additional source of alkalinity had an additional effect of reducing the carbon dioxide consumption.

The initial step in evaluating the potential for reuse was to determine the composition of the stream leaving the anion vessel. Figure 5 presents the rejection of anions of interest for cooling tower makeup. Figure 6 depicts some of the same data, except the sodium hydroxide concentration is included.

During the sodium hydroxide introduction step, almost 70% of the SO_4^{2-} and 50% of the total Cl^- are rejected, but only 13% of the NaOH leaves during this period. During the slow rinse cycle (60 to 90 min), 87% of the NaOH and most of the silica is contained. Upon the onset of the fast rinse cycle, the recoverable sodium hydroxide concentration becomes negligible.

The ion balance then allows us to see the effect of reusing this water at the cooling tower. Table 5 shows that reuse of this water has negligible impact on the cooling tower chemistry.

Sodium hydroxide demand at the tower closest to the demineralizers was 34 to 68 gal/day (130 to 258 L/day) of 20% sodium hydroxide or 68 to 137 lb/day (30 to 62 kg/day) as sodium hydroxide. Recoverable sodium hydroxide from the rinse water came to over 780 lb/day (350 kg/day). The cooling tower chemistry is based on meeting the sodium hydroxide demand at that one tower.

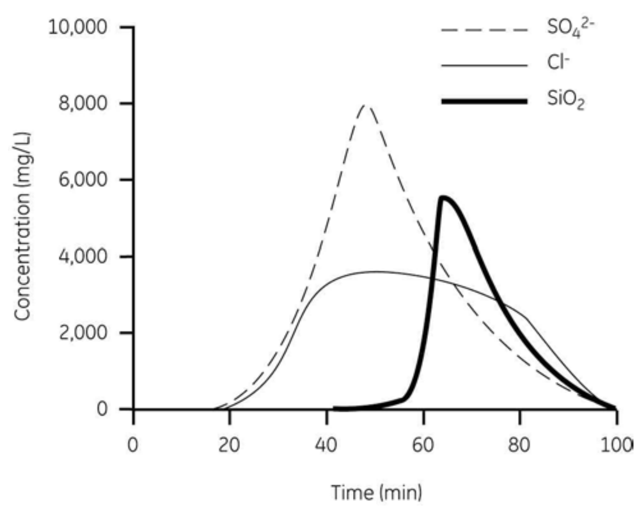

Figure 6: Demineralizer regeneration rinse water

Table 5: Cooling tower chemistry

Component	Lake Makeup	Rinse Water	Composite	Cooling Tower at Eight Cycles
Cl^- ppm (mg/L)	20	2,680	22	176
SO_4^{2-} ppm (mg/L)	21	2,370	23	184
SiO_2 ppm (mg/L)	8	2,310	10	80

Table 6: Boiler blowdown reuse

	Case 1	Case 2
Boiler Pressure	750 psig (53 kg/cm²)	900 psig (63 kg/cm²)
Steam Production	220 M lb/hr	900 M lb/hr
Boiler Cycles	50	100
Polymer in Boiler Blowdown	34 ppm (mg/L)	21 ppm (mg/L)
Blowdown as Percent Cooling Tower Makeup	1.6%	1.7%
Cooling Tower Cycles	11	15
Cooling Tower pH	8.4	8.5
Boiler Polymer Concentration	6.3 ppm (mg/L)	5.2 ppm (mg/L)
Cooling Polymer Concentration	12.1 ppm (mg/L)	11.7 ppm (mg/L)
Cooling Tower Calcium	900 ppm (mg/L)	600 ppm (mg/L)
Ratio of Cooling to Boiler	1.92	2.25

Use of Boiler Blowdown as Cooling Tower Makeup

Use of boiler blowdown as cooling tower makeup is another reuse scheme that has been employed at a number of locations. The primary concern when employing this technique is the interaction of polymers used as dispersants in boiler water and the polymers used as dispersants in cooling water systems. Operating data from two locations reusing boiler blowdown is given in Table 6.

Table 7: Cooling tower chemistry after boiler blowdown*

Sample	Unfiltered vs. Filtered Phosphate	Cooling Tower Polymer	Estimated Polymer Ratio	Results
Before Boiler Blowdown	0.2 ppm (mg/L)	9.0 ppm (mg/L)	—	Good Corrosion; No Deposition
After Boiler Blowdown	4.0 ppm (mg/L)	9.0 ppm (mg/L)	2.5	Deposition; Pitting

* Recirculating water conditions were: Ca+2 = 400 mg/L, Mg+2 = 200 mg/L, pH = 7.4, and conductivity = 2,600 µmhos.

Both of the operating boilers use mixed bed demineralized water as makeup, hence high cycles and low blowdown flow. However, the cooling towers also run at relatively high cycles of concentration, so the ratio of cooling polymer to boiler polymer at both locations is approximately 2:1. With the calcium levels present in the recirculated water, the polymer levels are considered normal. The polymer used in the boilers is a polymethacrylate, while the cooling tower polymer is an acrylic acid/allyl hydroxyl propyl sulfonate ether. The cooling polymer is effective in preventing calcium phosphonate precipitation. No interference in the ability to prevent this precipitation was observed in either case.

One of the other measures of polymer/polymer interference is the ability of the cooling tower polymer to maintain soluble phosphate ion in the recirculating water. An indicator that any particular polymer has lost some of its efficacy is the presence of precipitated phosphate in the water. Field tests run on filtered (0.22 µm) vs. unfiltered water samples can provide this measure.

Table 7 depicts the data from a cooling tower that was receiving boiler water blowdown as makeup. The boiler polymer was polymethacrylate, however the cooling water polymer was a copolymer of acrylic acid and hydroxyl propyl acrylate. The ability of this particular cooling polymer to work effectively was diminished by the presence of the methacrylate.

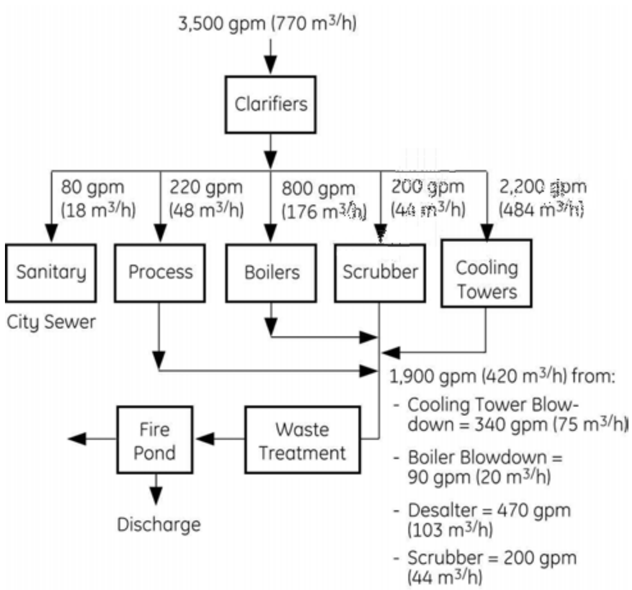

Figure 7: Water Balance

Table 8: Wastewater Analysis

Component	Concentration
pH	7.1
Conductivity	4,830µmhos
SO4–2	1,980 ppm (mg/L)
Cl–	471 ppm (mg/L)
Ca+2	163 ppm (mg/L)
Mg+2	93 ppm (mg/L)
Na+	1,150 ppm (mg/L)
PO4–3	2.0 ppm (mg/L)
SiO2	29 ppm (mg/L)
TOC	11 ppm (mg/L)

Limits of Water Reuse

Water reuse in an industrial environment involves taking water back for various uses somewhere in the process. Frequently, this use involves evaporation, which means an additional concentration of salts. When used as cooling tower makeup or as scrubber water makeup, various alternatives are available to minimize the effect of these high conductivity waters. These include chemical corrosion inhibitors, use of side stream softening, installation of different metallurgy, etc.

However, with the institution of whole effluent toxicity testing on many industrial dischargers, the impact that water reuse has on toxicity must be included in any water reuse plan. Many industrial facilities are mandated to use freshwater organisms, such as Daphnia magna, for effluent toxicity testing. Higher salinity levels in wastewater will cause osmotic stress to these organisms, so there is an antagonistic effect between compounds or metals in the wastewater and the salinity level. Water Quality Criteria[1] reports that the threshold concentration of sodium chloride for immobilization of Daphnia magna varies between 2,100 and 6,100 ppm (mg/L).

Increased water reuse causes the salinity level of the wastewater to increase. In the examples in this paper, the increase in salinity was the driving force behind waste minimization.

Table 8 shows the wastewater analysis for a Gulf Coast refinery that practices excellent water conservation measures. This refinery uses <20 gal/bbl (<76 L/bbl) crude oil, versus the industry average of 60 to 90 gal/bbl (228 to 342 L/bbl) crude[2]. Despite this, they were still interested in further conservation measures. The water balance is depicted in Figure 7.

Because of the excellent water conservation measures already in place, there were few opportunities for additional reuse. The opportunities that were evaluated included:

- Fire pond water as desalter wash water
- Rerouting of boiler blowdown to the influent clarifier
- Reusing fire pond water as scrubber makeup
- Reuse of fire pond water as cooling tower makeup

Each of these alternatives was evaluated based on the effects that water reuse would have on each individual unit operation. As an example, the use of fire pond water as scrubber makeup could eliminate 200 gpm (44 m^3/hr) of fresh water use with no deleterious effect on the scrubber water chemistry.

Unfortunately this option, as well as the others, was eventually eliminated from consideration because they all had the effect of increasing the salinity level in the waste discharge. Because of the effects of increased salinity on the whole effluent toxicity tests required at this facility, additional water reuse programs were deferred.

Summary

Water reuse/wastewater minimization opportunities exist in almost all industrial plants. The results from the reuse of secondary treated wastewater as cooling tower makeup indicate that good corrosion protection can be achieved when using a high conductivity water source. Attention must be paid to the variability of some of the constituents in the wastewater, particularly phosphate and calcium.

Reuse of demineralizer regenerant wastewater can take many forms — from reusing the spent regenerant in a subsequent regeneration to combining cation and anion regenerant wastes to provide neutralized waste waters as cooling tower makeup. Data was presented on a unique reuse scheme where the alkalinity of the anion regenerant was beneficial due to the feed of sodium hydroxide for cooling tower pH control.

Use of boiler blowdown as cooling tower makeup was also discussed. The compatibility of the various polymers employed should be determined before this technique is used.

When reusing water, whether within a process or reusing treated water, a holistic approach should always be taken. The effects of salinity on effluent toxicity may be the limiting factor when reusing water, instead of the water quality necessary for unit operations.

Acknowledgement

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Bibliography

1. McKee and Wolf, Water Quality Criteria, second edition, April, 1971.
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