

Reuse of wastewater for industrial cooling systems

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ABSTRACT: Reuse of municipal effluent for cooling systems in a large refinery and petrochemical complex is described. Quality criteria for the cooling water were related to scale formers, corrosion, and biogrowth. After tertiary lime treatment using sludge blanket precipitator-clarifier was applied, phosphate removal, high reductions in alkalinity, calcium, COD, and suspended solids were obtained. A stripping tower reduced ammonia concentrations by 50%. Biological nitrification eliminated ammonia in the circulating cooling system. Acidity generated by nitrification neutralized excess lime in treated effluent. Reclamation of wastewater for cooling saved millions of cubic meters of fresh water. *J. Water Pollut. Control Fed.* **60**, 237 (1988)

KEYWORDS: wastewater treatment, reuse, cooling systems, tertiary treatment, nitrification

Water shortages in semi-arid and arid areas require extensive wastewater reuse. Reuse, if properly planned, may also provide an economically efficient solution for water pollution control. The high cost of advanced treatment processes, giving high contaminant removal, can often be justified in reuse schemes through the high value of reclaimed water.

Cooling systems are major water consumers in many industries, therefore, using reclaimed wastewater for this purpose may bring considerable savings in fresh water consumption.

Treated wastewater usage for industrial cooling has been reported by others^{1,2} who have described the use of Amarillo, Tex., wastewater treatment plant effluent, after lime treatment, as make-up water for a refinery and a power plant cooling systems. Others^{3,4,5} reported on effluent use for cooling make up in South Africa and England.

This paper describes municipal effluent reuse in a large industrial plant cooling system. The water quality problems and processes in such systems, related to the characteristics of the reclaimed wastewater, are analyzed and discussed.

Water Quality Requirements

Before discussing quality considerations it is helpful to review the schematic flow diagram of a circulating cooling system (Figure 1). Details of material balance are discussed later. Briefly, concentrations of constituents in circulating cooling water are much higher than in the make-up water. Water quality requirements are related to three major problems encountered in circulating water cooling systems: scaling; corrosion; and biofouling.

Scaling factors. Calcium carbonate scale formers are present both in fresh water and reclaimed wastewater, but in wastewater these constituents are higher in concentration. Calcium phosphate scale formers are specific for reclaimed wastewater because of high phosphate content in such waters, whereas phosphates are not commonly found in fresh water supplies. Equilibria calculations show that phosphate concentrations commonly found in effluents, particularly when enhanced by concentration cycles in cooling systems, could be a strong scale-forming factor on heat exchangers surfaces.⁶

Corrosion factors. Total dissolved solids (TDS) including chlorides are a general corrosion factor present in freshwater and wastewater, the latter at higher concentrations. Their concentration in circulating cooling water is controlled by concentration cycles, for example, by blow-down. A corrosion factor specific to wastewater effluents is ammonia, which is corrosive to copper alloys frequently used in heat exchange systems.

Biofouling factors. Biofouling is encountered in most recirculating cooling systems, but when reclaimed wastewater serves as make-up, biogrowth may be enhanced because of residual organic substrate and high nutrient content N and P.

Renovation of Effluent for Reuse

The industry complex studied includes a petroleum refinery, and several petrochemical and chemical plants with an interconnected water-cooling system. With new plant developments, extensions and production increases in the early 1970s, two natural draft cooling towers in the refinery reached an overtower recirculation rate of 25 000 m³ h⁻¹ and several smaller forced-draft towers in the connected industrial plants worked at a total recirculation of 5000 m³ h⁻¹. The make-up water requirement to this system was about 500 m³ h⁻¹ mounting to an annual consumption of 4 million m³. Although supplying this much water from fresh water sources posed serious problems in this water short area, a municipal wastewater treatment plant, located approximately one mile from the industrial complex, produced about 14 million m³ of trickling filter effluent annually, of which only a few million m³ were then used for cotton irrigation in nearby farms. Reusing this effluent as a source for make-up to the industrial cooling system was then considered.

The quality and composition of the secondary effluent

RECIRCULATING COOLING SYSTEM

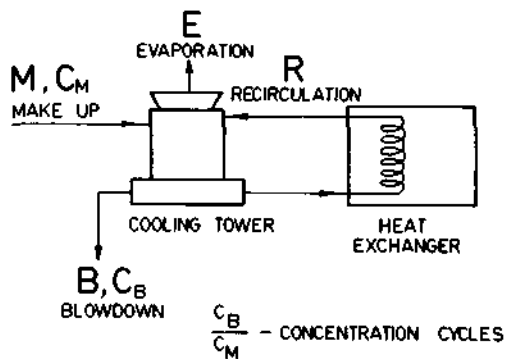


Figure 1—Recirculating cooling system.

can be seen in Table 1, where also the raw wastewater characteristics are shown. The effluent is relatively high in COD, ammonia, phosphorus, and alkalinity as well as in total salinity and chlorides—all important factors when considering use as cooling make-up water. The relatively high concentrations of these constituents in the effluent is caused by the low per capita water use because of water shortage in the country. Quality requirements were related in scaling, corrosion, and biofouling, factors that were previously discussed.

Tertiary Treatment

Because of secondary effluent characteristics, tertiary treatment was considered to be necessary. The treatment objectives were removal of ammonia and phosphates, reduction in alkalinity (biocarbonate) and calcium, and reduction in suspended solids (SS) and organic content (COD).

The preconceived treatment scheme to meet those objectives included the following unit operations and processes: high lime precipitation-clarification, ammonia stripping, and pH adjustment.

Bench scale studies of effluent lime treatment were undertaken. The results indicated that low phosphate residual and high clarification can be achieved at lime doses that raise the pH to above 10.5 where magnesium hydroxide precipitates. Magnesium hydroxide acts by an adsorption-

flocculation mechanism and by sweeping as a flocculant for colloidal phosphates, particulates, and organics.

A full scale trial period was then initiated. An existing sludge-blanket type precipitator-clarifier was used for lime treatment and a reserve forced-draft cooling tower was used for ammonia stripping. The tertiary-treated effluent was then supplied as make-up water to the cooling system. The flow sheet of the full scale treatment system is shown in Figure 2.

The tertiary treatment performance and the circulating cooling water (CCW) quality can be seen in Table 1. Almost complete phosphate removal and high reductions in SS, BOD, calcium, and alkalinity were obtained in the lime treatment. Ammonia reduction in the stripping tower was 40 to 60%. Ammonia stripping was accompanied, as expected, in a reduction in alkalinity equivalent to NH_3 stripped. Chemical tertiary treatment performance was satisfactory in meeting treatment objectives except for only partial ammonia removal in the stripping tower.

Nitrification in the Recirculating Cooling System

While the stripping operation has left significant ammonia concentrations, essentially complete ammonia elimination was observed in the cooling system. Ammonia elimination in the cooling system could be by stripping in cooling towers or biological nitrification. Relatively high nitrate concentrations in the CCW indicates that a great part of ammonia reduction was accomplished by biooxidation to nitrates by nitrification. Also, the reduction in pH from 10.5 in precipitator effluent (make-up water) to 7.8 in circulating cooling water, without any acid addition, confirms that nitrification takes place in the system. As shown from the nitrification process equations, two moles of acid are produced per mole of nitrate formed.

Nitrification Reaction Equations

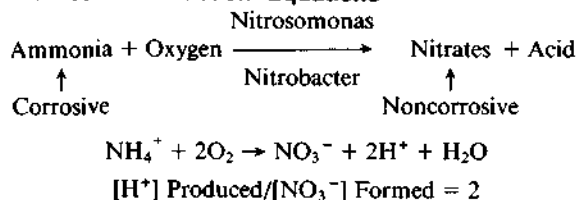


Table 1—Analysis of raw wastewater, secondary and tertiary effluents, and circulating cooling water. (average values.)

Component	Unit	Raw wastewater	Secondary effluent	Tertiary effluent	Circulating cooling water
pH			7.2	10.5	7.9
Alkalinity	mg/L as CaCO_3		620	250	300
Hardness	mg/L as CaCO_3		450	150	250
Chlorides	mg/L		350	350	500
Suspended solids	mg/L	400	60	15	30
BOD_5	mg/L	450	50	10	<5
COD	mg/L	950	240	80	110
Ammonia	mg/L	60	35	25 (11) ^a	<1
Nitrate as N	mg/L	nil	2.2	2.2	13.6
Phosphate	mg/L	30	20	0.2	0.1

^a After ammonia stripping tower.

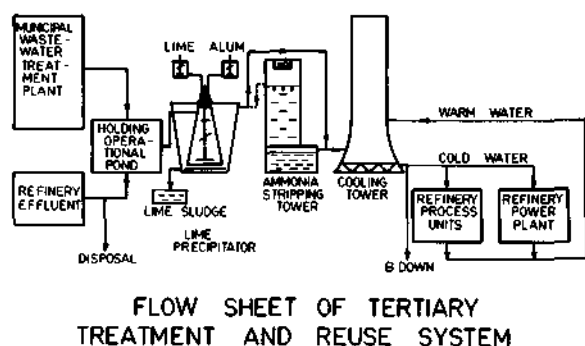


Figure 2—Flow sheet of the tertiary treatment and reuse system.



Nitrification in cooling systems accompanied by reduction in alkalinity, was observed also by Osborne³ and Humphris.⁵ The acidity produced in the nitrification process serves for neutralization of the residual hydroxide and carbonates present in the precipitator effluent supplied to the recirculating system. In this way, the nitrification process provides a self-regulating pH control mechanism without the need of external acid addition.

When reclaimed wastewater is low in alkalinity the nitrification taking place in a cooling system may result in acidic conditions and have corrosive effects because of low pH values. That situation is expected when the equivalent ratio of alkalinity to ammonia is below 2. This was the reason for the low pH and corrosive effects observed by Osborne³ in his cooling system. Because of carbonic acid produced in the neutralization reaction and its equilibria relationships with bicarbonate, lower than desired pH values may be obtained when alkalinity to ammonia ratios are only slightly higher than 2. Therefore, in practice, whenever the ratio $\text{Alk (eq/L)}/[\text{NH}_4^+]$ is lower than 3, nitrification in cooling system should be considered as undesirable and the reclaimed wastewater should be nitrified before supplying it for cooling system make-up. Ammonia oxidation to nitrates eliminated the ammonia corrosion problem. Unlike ammonia, nitrates are not corrosive to copper alloys, they may even have a beneficial effect, acting often as a corrosion inhibitor to many metals.

Nitrification and complete elimination of ammonia in the recirculating cooling system was taking place also after the stripping tower was bypassed. Therefore, after a few weeks of trials, stripping tower operation was discontinued and since then the lime precipitator effluent has been fed directly as make-up to the cooling system. Ammonia elimination and nitrification during a 14 month period can be followed in Figure 3. While ammonia in precipitator effluent was from 5 mg/L to 45 mg/L and nitrates were usually less than 2 mg/L, the ammonia content of CCW was below 1 mg/L and nitrates as N averaged around 15 mg/L.

The recirculating cooling system seems to be a reliable and efficient nitrification reactor, because of the following favorable conditions for the nitrification process:

- plentiful oxygen supply in the cooling towers;
- favorable and constant temperatures;
- low specific organic load; and
- long cell residence time of the attached growth (the attached growth comprises more than 80% of total biomass and its average residence times can reach a few weeks⁷).

Biofouling

Biogrowth was observed, both in the form of attached biomass and dispersed as organic ss. A separate research project has been conducted on a pilot-plant scale and its findings, such as kinetics and yields, will be a topic of a separate paper. A large part of the biogrowth is ascribed to reusing the refinery's own effluent, which has a much higher organic substrate content than renovated municipal effluent. In general, biofouling can be controlled by using biocides such as chlorine, a procedure practiced in many cooling systems, including those reusing effluents. Where nitrification in the cooling system is beneficial and desired, this procedure cannot be applied. Biofouling must be controlled through more frequent cleaning operations of heat exchangers or through better pretreatment of the reclaimed wastewater. This procedure reduces the organic substrate concentration responsible for the biogrowth to an economical minimum. Also, sidestream treatment can be applied for suspended growth. Before deciding on biofouling control strategies, an economic analysis of the options is recommended. The costs and benefits of additional heat exchangers cleaning to enable nitrification in the cooling system when biocides are not applied should be compared to the cost of biocides applications plus the cost of nitrification as a pretreatment process.

Salinity, Chlorides and "Replacement Ratio"

For each recirculating cooling water system, limiting concentrations of chlorides and TDS are set above which

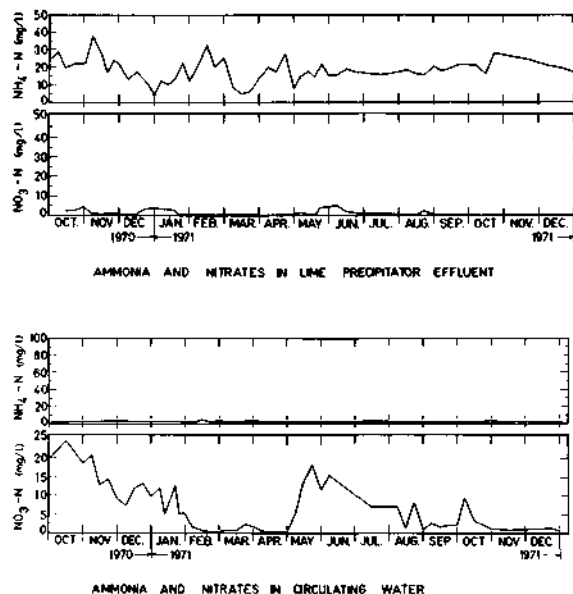


Figure 3—Ammonia and nitrates in precipitator effluent (make-up water) and in circulating cooling water.

corrosion effects may be expected. The relationships between blow-down rate, concentration in make-up water, and concentration in CCW can be shown through a material balance across the cooling system (Figure 1). The flow and material balances are summarized in Equations 1 to 5.

$$M = E + B \tag{1}$$

$$MC_M = E \cdot O + BC_B \tag{2}$$

$$C_B + C_M = 1 + E/B \tag{3}$$

$$B = E(C_B/C_M - 1)^{-1} \tag{4}$$

$$M = E[1 + (C_B/C_M - 1)^{-1}] \tag{5}$$

M, *E*, and *B* are the make-up, the evaporation, and the blow-down rates, respectively. *C_M* and *C_B* are, respectively, concentrations in the make-up and CCW. Concentrations in blow-down and CCW are essentially identical. The ratio *C_B/C_M* is defined as concentration cycles in cooling water terminology.

For a given evaporation rate *E* (given thermal load) the make-up rate is governed by blow-down requirements related in turn to concentration cycles. A given limiting concentration *C_B* of a constituent in the cooling water can be maintained by controlling the blow-down rate *B* and the concentration of the constituent in question in the make-up water *C_M*. The control of *C_M* is limited to economically treatable constituents only. The control (reduction) of chlorides and TDS in make-up water, which can be accomplished by one of the desalination processes, is considered too costly at this stage. Therefore, chlorides and TDS in the CCW are being controlled by blow-down. The salinity and chloride concentrations in reclaimed wastewater, used as make-up, are always significantly higher than in fresh water supplies in the same area. For a given limiting chloride content in the CCW (*C_B*), the higher chloride content in the make-up (*C_M*) requires the ratio (*C_B/C_M*) to be lower. This implies that concentration cycles (*C_B/C_M*) for renovated (reused) wastewater have to be lower than for fresh water. Lower concentration cycles require higher blow-down and consequently higher make-up as can be seen from Equations 4 and 5. For this reason, the make-up consumption of renovated wastewater is always higher than fresh water. The ratio of renovated water make-up consumption to fresh water consumption is defined as replacement ratio.

$$R_r = M_S/M_F$$

Where:

R_r = replacement ratio.

M_S = make-up consumption of renovated wastewater, and

M_F = make-up consumption of fresh water.

The replacement ratio *R_r* depends mainly on the ratio of chlorides in wastewater to chlorides in fresh water.

$$r = \frac{C_S}{C_F} = \frac{\text{chlorides in wastewater}}{\text{chlorides in fresh water}}$$

Through mass balance considerations, an expression was derived for calculations of *R_r*. The expression relates

the replacement ratio *R_r* to the ratio of wastewater to freshwater chlorides *r* and to the limiting chloride level in CCW, the latter expressed in a normalized manner as *C_B/C_F*.

$$R_r = \frac{(C_B/C_F) - 1}{(C_B/C_F) - r} \tag{6}$$

Replacement ratios *R_r* for various wastewater to freshwater chlorides ratios *r* = *C_S/C_F*; are plotted in Figure 4 versus limiting chlorides in CCW expressed in terms of *C_B/C_F*.

The replacement ratio has to be taken into consideration in cost analysis of reclamation systems. Replacement ratios exist also in agricultural reuse schemes, based on somewhat different considerations but related also to salinity and chlorides.

Reuse and Aquatic Environmental Quality

The tertiary treatment and the reuse of the effluent in the cooling system has been continued for many years, resulting in great fresh water savings. Part of the refineries' own process wastewater has been also reused via the same treatment route.

The blow-downs from the recirculating water systems are usually discharged to receiving waters. It can be seen from Table 1 that the blow-down is superior, in most water quality parameters, to the secondary effluent. Phosphate content is very low, ammonia was completely oxidized to nitrates, the total nitrogen is much lower than in secondary effluent, and the organics are highly oxidized. Chlorides and TDS however, are, higher in the blow-down than in the secondary effluent. Their concentration depends on the concentration cycles applied in a given system. In general, the discharge of cooling water blow-down from a system using reclaimed effluents is an environmentally preferable discharging secondary effluent. The better quality of CCW is achieved through advanced treatment, which could be economically justified by the value of the reclaimed water, and through the beneficial bio-oxidation processes in the cooling system itself. The latter are possible

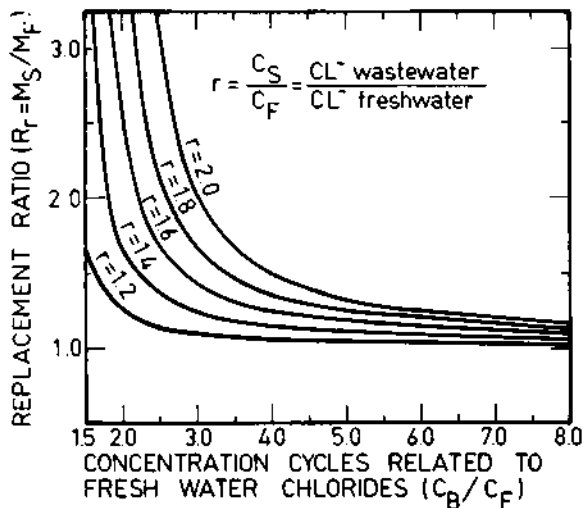


Figure 4—Replacement ratio: ratio of renovated water to fresh water consumptions for make up.

only if chlorination or other biocide treatments are not practiced. This in itself is environmentally desirable to avoid formation of objectionable chlorinated organics.

Wastewater reuse for industrial cooling systems, if properly designed and operated, may contribute to better aquatic environmental quality control.

Summary and Conclusions

Wastewater renovation for industrial use has significant advantages and recirculating cooling systems are prime candidates for renovated effluents usage. Quality criteria for this use relate to scaling, corrosion, and biofouling agents.

A municipal secondary effluent has been successfully reused as make-up water to a large circulating cooling system in a refinery and petrochemical complex. Tertiary lime treatment removed phosphates, reduced alkalinity (bicarbonate), and calcium, which reduced major scale formers and significantly reduced organic input into the system. Ammonia was completely bio-oxidized to nitrates in the circulating cooling systems, solving the ammonia corrosivity problem to copper alloys. Acid produced by bionitrification served for neutralization of excess lime supplied with the lime precipitator effluent, no external acid addition was necessary. The industrial circulating cooling systems are efficient nitrification in such systems. To enable bionitrification, chlorination or other biocide treatments should not be applied. Biogrowth, which may occur, can be controlled by mechanical cleaning, side-stream treatment or it can be reduced by better biological pretreatment that removes most organics that serve as substrate for biogrowth. Wastewater effluents are of higher chloride and mineral salinity content than fresh water supplies in the same locality. This implies lower concentration cycles in the cooling system operation, higher blow-downs, and consequently higher make-ups than in the case of fresh water supplies. The ratio of reclaimed wastewater make-up to fresh water make-up was defined as replacement ratio and an expression was derived enabling calculation of the replacement ratio as a function of wastewater chloride to fresh water chloride ratios and limiting chlorides in the cooling water system. The blow-down from cooling systems using reclaimed effluents is of general better water quality than the effluent before reuse. The pollutional loads of such blow-down discharges is signifi-

cantly lower than the load of secondary effluents (except for chlorides and mineral salinity). In general, reuse contributes to better environmental and water pollution control, in addition to very significant resource conservation.

Acknowledgments

Credits. Judy G. Brown of Virginia Polytechnic Institute and State University helped in correcting the English and the typing of this manuscript.

Authors. This manuscript was revised and rewritten by M. Rebhun when serving as a visiting professor with the Department of Civil Engineering, Virginia Polytechnic and State University, Blacksburg, Va. At the time the original work was performed, G. Engel was an environmental and water development engineer with Oil Refineries Ltd. Menahem Rebhun is a professor of Environmental and Water Resources Engineering, Technion-Israel Institute of Technology, Haifa, Israel. Gideon Engel is the head of the Safety Division, Oil Refineries Ltd., Haifa, Israel. Correspondence can be sent to M. Rebhun, EAWAG, Dubendorf CH-8600, Zurich, Switzerland.

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