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Economical and reliable mercury reduction in refinery and power plant discharge wastewater with robust microfiltration membrane technology

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ABSTRACT

Environmental concerns and risks to bioaccumulation of mercury components among aquatic organisms, thus finally through the food-chain, and therefore exposing human health potentially, lead to more stringent regulations over the last years in several regions across the globe. Mercury (Hg) is a key contaminant in several crude oils and coal. Most of the mercury appears to exist in suspended and adsorbed forms and there is also the dissolved component in the form of methylmercury and salts. As an example, the United States EPA's Great Lakes region initiative targets limiting the total mercury in lakes and streams to 1.3 nanogram/l (ppt). Many states in the USA along the Great Lakes and the Ohio valley limit total mercury in discharge wastewater to 12 nanogram/l (ppt) already. Western Europe and parts of Asia are most likely to implement similar mandates in the next few years. This paper describes in the first case a lengthy and successful plant trial performed by Pall Corporation on discharge wastewater generated at a refinery in the USA. Microfiltration (MF) systems were employed to treat the end of pipe wastewater after it goes through conventional treatment processes such as API separator and biological reactor treatment. The total mercury was reduced to below 5 ppt in the permeate from the MF process without the aid of additives or post treatment, thus reducing 90% of the total mercury in the feed to the MF system. The target levels were met consistently and the automated system ran smoothly. Independent of huge variability of the feed turbidity and changing mercury levels, the hollow-fiber system showed stable and reliable operation for more than 12 months under "real" site conditions. Above innovative approach eliminates the need for further mercury polishing steps while reaching target levels with a very solid and proven high-crystalline PVDF hollow fiber, that collect solids and contaminations only on the outer membrane side, which enable easy regeneration and cleanability all the time. The second case study refers to the power generation industry. Wet flue gas desulfurization (FGD), used primarily to control SOx in coal-fired power plants, also captures the Hg in its various forms. The wastewater generated in this process is

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contaminated accordingly, thus needing treatment for Hg removal before discharge to the environment. This second case study discusses experimental work done by Pall for the removal of Hg from FGD wastewater as a final polishing step, with and without chemical precipitation followed by MF to remove the Hg captured in the precipitate. Stable and positive results from both case studies could be obtained, hence proving that high crystalline PVDF in hollow fiber membranes is a simple, reliable, long-term and cost economic solution for the reduction of mercury compounds in wastewaters.

Keywords: Mercury removal; Environmental protection; Wastewater; Membrane systems; High crystalline PVDF; Discharge water; Hollow fibers; Toxic components removal

1. Introduction: mercury in wastewaters of energy industries

Mercury is an extremely rare element in the Earth's crust and has an average crust abundance of 0.08 ppm by mass [1]. While natural sources such as volcanoes are responsible for approximately one-half of atmospheric mercury emissions, human activities, especially related to the production of fossil fuels and energy (e.g. refineries and coal-fired power plants), also significantly contribute to the global mercury budget.

Mercury emissions associated with energy industries are mainly in wastewater and flue gas from refineries as well as from coal-fired power plants. Flue-gas treatment such as desulfurization transfers the mercury into the wastewater streams from these power plants. Due to the high toxicity and tendency of bioaccumulation of mercury in the aquatic food chain, environmental regulations in the USA have become increasingly stringent with respect to mercury. Many such regulations restrict the discharge limit of mercury to the level of parts per trillion (ppt). The maximum contaminant level (MCL) for drinking water in the USA is 2 μg/L based on induction of autoimmune kidney diseases [2]. Therefore, the discharge limit for mercury in wastewater streams is in the order of magnitude lower than the drinking water standards, primarily due to the concerns of its accumulation through food chain.

Most of the mercury in refinery wastewater is originated from crude oil. It is estimated that the concentration of mercury in the crude oil is close to 10 ppb and the total amount of mercury in US petroleum production is calculated as 17,600 lb/y [3]. There is little information on the species of mercury in the crude oil, it could be in various inorganic and organic forms and the majority of mercury is likely to end up in the spent wash water (i.e. or brine) from desalter. The distribution of mercury compounds in petroleum samples varies widely. The amount and relative distribution of mercury compounds in liquid hydrocarbons depend on the sample source and history. Crude oil and unprocessed gas condensates contain significant amounts of suspended mercury compounds, mostly mercuric sulfide. The dominant dissolved species in petroleum are elemental mercury and ionic halides. Ionic mercury compounds have been found in significant proportions in liquids, but it is not known if they are abundant naturally or if they exist due to post-collection conversion of other mercury species [4]. Most of the mercury in the petroleum can eventually enter wastewater stream via various processing processes, especially desalting and desulfurization.

For mercury emission associated with flue gas of coal-burning power plants, the mercury concentration varies considerably with the grade and origins of coals. Wet scrubber for flue gas desulfurization transfers mercury from gas into the spent scrubber wastewater. In addition, water discharged from ash ponds also contributes to mercury concentration. Because various factors contribute to the mercury concentration in the wastewater from coal-fired power plants, it can vary from tens of micrograms per liter (ppb) to tens of nanograms per liter (ppt). There is no data on the speciation of mercury in these wastewater streams.

2. Mercury chemistry

The most stable inorganic Hg species in nature are elementary mercury (Hg^0) or divalent mercury (Hg^{2+}). Because the standard redox potential for Hg is relatively low (0.65–0.85 volt) and Henry's constant for Hg^0 is relatively high, Hg^0 is unlikely to be the predominant species in a well-oxygenated water such as secondary effluent from a wastewater treatment plant in a refinery. Theoretical calculations indicate that the predominant Hg species are $Hg(OH)_2$ and $HgCl_4^{2-}$ in (oxygenated) fresh water and seawater, respectively [5].

Hg^{2+} can form a complex with various anions. It also forms precipitates with hydroxide, carbonate, and bromide. Thermodynamically, mercury hydroxide precipitates are more stable than various complexes of Hg^{2+} and hydroxide, as indicated by the values of equilibrium constants in Table 1.

As indicated in Table 1, $Hg(OH)_2$ (s) is a predominating species at equilibrium, in lieu of lacking other strong ligands for mercury. For comparison purpose, the equilibrium of $HgCO_3$ (s) is also listed in Table 1. In an aquatic environment with high alkalinity, $HgCO_3$ (s) is also expected to be present.

Another common form of mercury is methylated mercury ($CH_3–Hg^+$), or methylmercury. Methylmercury is formed in aquatic environment by the action of anaerobic microorganisms. Methylmercury is a positively charged ion that readily combines with anions such as chloride, hydroxide, or nitrate. When combined with anions, methylmercury is dissolved in water. Methylmercury has a high affinity for sulfur-containing anions, especially the thiol group (–SH) in cysteine (an amino acid). Adsorption of methylmercury by proteins containing thiol group is considered as the main mechanism of mercury enrichment in the aquatic life food chain. This is the reason why methylmercury is more toxic than other mercury species.

Based on mercury chemistry discussed above, a model of reactions governing mercury species in oxygenated water and sediments is proposed as depicted in Fig. 1.

As indicated in Fig. 1, (at equilibrium) the majority of inorganic mercury species is in the form of Hg $(OH)_2$ (s), while methylated mercury accounts for the larger part of dissolved Hg species. The percentage of dissolved inorganic Hg species is likely very small because of low solubility of those species. Implication of this model is that a significant portion of inorganic mercury Hg species in well-oxygenated water is in the form of solids and can be removed by filtration.

Because of the chemical nature of different Hg species, the source of wastewater and wastewater treatment processes can exhibit different Hg removal rates. *For refinery wastewater*, the typical treatment processes include oil–water separation, dissolved air flotation (DAF), and biological treatment. This leads to a very low level of Hg concentration in the treated effluent (sub-ppb level). It is possible that some of the methylmercury may be removed in the biological process by its adsorption to thiol-containing proteins in extracellular polymeric substances (EPS). On the other hand, *wastewater from coal-fired power plants* is typically treated by coagulation or lime-softening, clarification, and filtration. Therefore, not only the quantity, but also the speciation of mercury from different sources can be rather different.

Table 1
Equilibrium constants of various reactions of Hg^{2+} and hydroxide (25℃)

Reaction	Equilibrium constant (log)*
$Hg^{2+} + OH^- = HgOH^+$	10.6
$Hg^{2+} + 2OH^- = Hg(OH)_2$	21.8
$Hg^{2+} + 3OH^- = Hg(OH)_3^-$	20.9
$Hg^{2+} + 2OH^- = Hg(OH)_2$ (s)	25.4
$Hg^{2+} + CO_3^{2-} = HgCO_3$ (s)	19.8

*data are from [4].

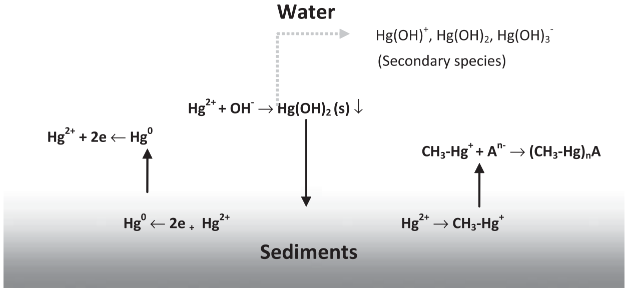

Fig. 1. Mercury species in water and sediments. (Vertical arrows indicate the migrations of species; dotted line indicates secondary reactions).

3. Treatment processes for mercury removal from wastewater

Conventionally, the treatment processes for mercury removal include lime-softening, electrodialysis/electrodialysis reversal (ED/EDR), and reverse osmosis (RO). Lime-softening is mainly limited to the removal of inorganic mercury, while ED/EDR and RO both are desalination processes and not practical for mercury removal from wastewater. Ion-exchange is also used to remove mercury primarily from certain industrial wastewater (e.g. mining wastewater), where mercury is mostly cationic [6]. Biological treatment such as activated sludge process can remove mercury by adsorbing it on the flocs. Adsorption by activated carbon also can remove mercury from water stream. However, the mercury removal by those two processes is always “accidental” because main functions of those two processes are for the removal of other contaminants from the wastewater. Absorbents such as zeolites, activated aluminum, and diatom earth have been used for mercury removal [7–9]. The removal mechanism of zeolites was found to be ion-exchange on negatively charged sites resulting from Al^{3+} replacement of Si^{4+} in the tetrahedral structure that have cages and cavities created by weakly held cations. Some absorbents are impregnated with sulfur to enhance the adsorption, as mercury has a high affinity to sulfur groups [10]. Due to competition from other cations in the water, it is not expected that this type of technology would achieve a mercury level in ng/L (ppt) practically.

The application of low-pressure membranes, i.e. microfiltration (MF) and ultrafiltration (UF), provides another option for mercury removal [11]. The pore size rating for MF and UF typically used in water filtration ranges from 0.02 to 0.2 µm. As indicated in Table 1, (inorganic) mercury can form precipitates with hydroxide and carbonate. As long as the size of the particles of those precipitates is above the pore size of membranes, the removal of those particles is nearly complete. The removal efficiency of methylmercury by low-pressure membrane is not well understood and is likely to be poor due to the fact that methylmercury tends to remain truly "dissolved" in the solution.

For low-pressure membranes, the removal efficiency of mercury depends upon speciation and the size distribution of mercury species in the water. A filtration test with various ratings of membrane pores conducted with a wastewater sample from the clarifier effluent of a wastewater treatment process from a refinery is presented in Fig. 2.

As indicated in Fig. 2, a 10 µm filter removed Hg by nearly 60% from the wastewater sample. As the pore size decreases, the Hg removal increases rather gradually. For example, Hg removal for 0.45 µm filter (the operating definition for "dissolved" species in water analysis) and 0.1 µm filter is 69 and 77%, respectively.

Fig. 3 compares Hg removal by a MF filter (0.1 µm) and an UF filter (WMCF = 80 KD, or 0.02 µm) for another wastewater sample from the same source as in Fig. 2. The results indicate that there is no statistical difference in terms of Hg removal with the two filters–both filters removed Hg by 95% approximately.

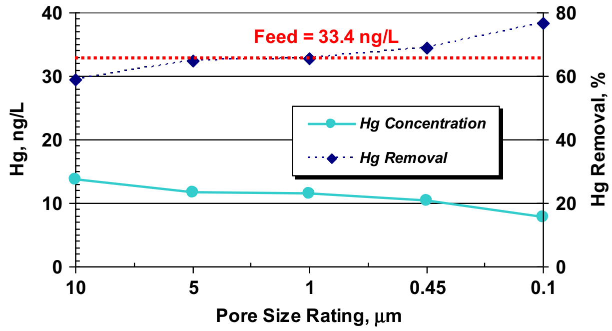

Fig. 2. Mercury removal as a function of membrane pore size rating of flat sheet membrane discs.

When comparing the results in Figs. 2 and 3, the difference in removal efficiency is very significant, considering the samples were from the same source, but at different sampling times. Two factors might have contributed to this difference: (1) the Hg concentration in Fig. 2 was much lower than that in Fig. 3; (2) different membranes were used in two figures: flat sheet membrane discs were used in Fig. 2, whereas hollow fiber membranes were used in Fig. 3. Considering the fact that Hg concentrations in filtrates in two figures are very similar, it is speculated that there was low concentration of truly "dissolved" Hg in both samples, and membrane filters would not be able to remove them.

Source water and pretreatment have significant impacts on Hg removal efficiency by low-pressure membranes. Pretreatment not only reduces Hg concentration, but also converts Hg from dissolved form to particulates, therefore enhancing the removal by suitable low-pressure hollow fiber membranes.

Due to high affinity of mercury for sulfur-containing compounds, a recent development is the application of polymeric organosulfide (i.e. polyorganosulfide) to remove Hg and other metals. Those polymeric organosulfides are water soluble but form precipitates with some metals. The sulfur functional groups may vary with different manufactures, but could be dithiocarbamate (RR″–N–CS_2–R′) or thiol (R–SH). The former forms octahedral complexes with metal, and the latter forms thiolate. Depending on the molecular structure, some polymers favor monovalent metals over divalent metals. Among the divalent metals, the order of affinity polyorganosulfide to transitional metals is as follows [12,13]:

$$Hg > Ag > Cd > Cu > Pb > Zn > Co > Ni$$

Due to the presence of multiple metal ions in wastewater, it is not practical to determine the

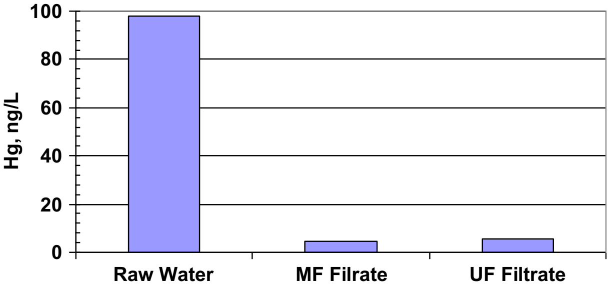

Fig. 3. Comparison of Hg removal by MF (0.1 µm) and UF (~0.02 µm) hollow fiber membranes.

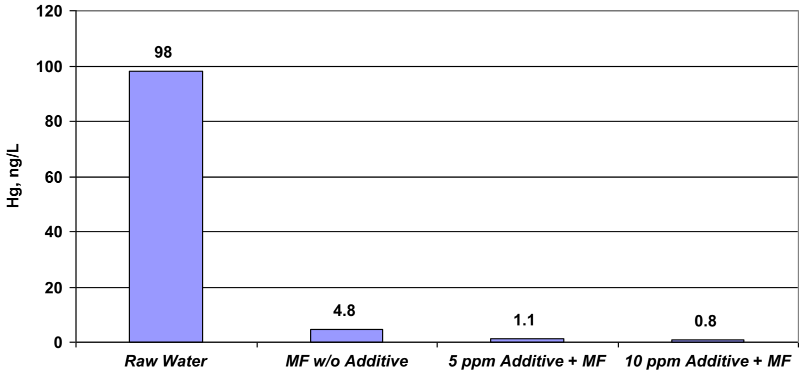

Fig. 4. Hg concentration remaining in the filtrate of 0.1 μm MF as a function of the dose of polyorganosulfide. Hg in raw water = 98 ng/L.

dose–Hg removal relationship simply based on the stoichiometry because the types of the metals, their concentrations, and affinity to polyorganosulfide vary. A jar test in conjunction with a filtration test may provide a practical tool for dose determination, as illustrated in Fig. 4.

The results in Fig. 4 indicate that the addition of 5–10 mg/L of polyorganosulfide could reduce Hg concentration in the filtrate to below 1 ng/L. The nonlinear dose–Hg concentration curve seems rather typical for the test of Hg removal with the addition of polyorganosulfides [13] and reflects the competition of other metals for the polymer.

Low-pressure membrane can provide the stable effluent quality with respect to mercury. The result from a pilot test with a production-scale 0.1 μm microfiltration membrane is summarized in Table 2 in which two sources of raw wastewater were tested.

As indicated in Table 2, the MF filtrates showed nearly identical average concentrations, although the average concentration in the feed of Source B is almost one order of magnitude higher than that in the feed of Source A. The results of the pilot tests are comparable with those of the bench tests in Figs. 2 and 3.

Table 2
Summary of pilot test results for Hg removal from refinery wastewater.

	Hg in the feed to MF (ng/L) (mean ± std. dev. /no. of samples)	Hg in the MF filtrate (ng/L)* (mean ± std. dev. /no. of samples)
Source A	17.4 ± 7.6/39	3.3 ± 1.0/41
Source B	150 ± 175/18	3.2 ± 2.0/17

*No chemical addition to the feed to either test.

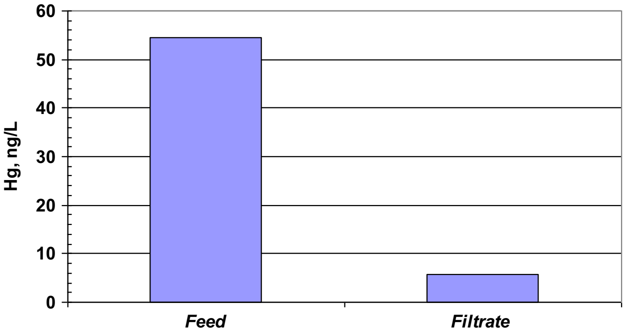

Fig. 5. Bench filtration test results for Hg reduction of the clarified FGD effluent.

Fig. 5 presets the result of a bench filtration test performed on the clarified effluent of the flue gas desulfurization (FGD) unit of a power plant using 0.1 μm filter without addition of polymeric organosulfides.

Again, the result indicates significant Hg reduction (~90%) simply by microfiltration.

A bench-scale test was conducted for FGD blowdown water containing high concentration of Hg that went through several treatment steps as shown in Fig. 6. Water samples were taken at various points of the process train: after the thickener of magnesium softening (A); after the Pond I (B); and after waste pond (C). Each sample was filtered directly, or with the addition of 5 ppm of an organic-sulfide precipitant. The results of the test are shown in Fig. 7.

The thickener effluent (A) of magnesium softening had a mercury concentration of 29 ppt. The mercury concentration continued to decrease after Pond I and Pond II to 6.5 and 1.8 ppt, respectively. Filtering with 0.1 μm membrane for the thickener effluent of magnesium softening, ponds I & II effluents reduced mercury concentration to 22.5, 3.1, and 1.8 ppt, respectively, resulting a removal of 22, 32, and 0%,

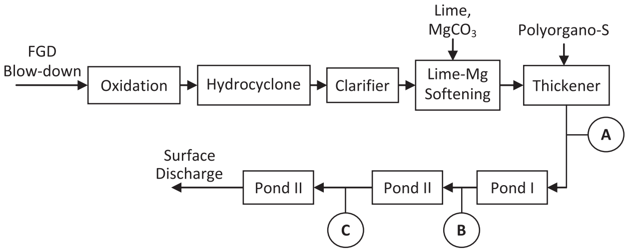

Fig. 6. Schematics of FGD blow-down treatment and sampling points for the test.

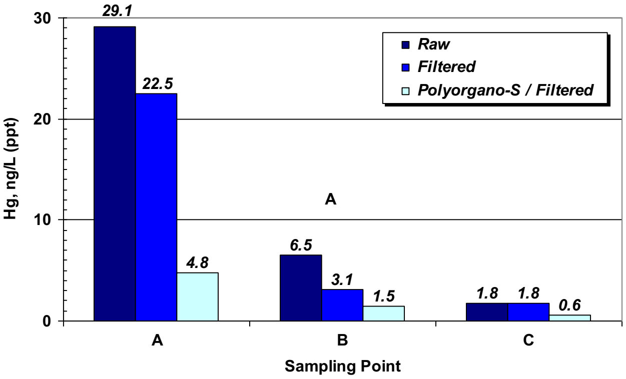

Fig. 7. Mercury removal of FGD blow-down after various treatment stages by microfiltration with and without addition of organic-sulfide precipitant.

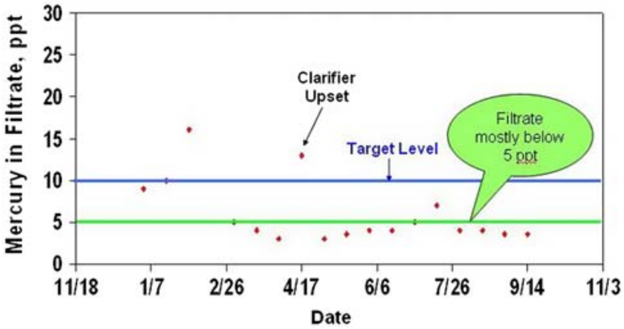

Fig. 9. Hg concentration in a Pall Aria microfiltration system during a pilot test of refinery wastewater.

respectively. With the addition of 5 ppm organic-sulfide precipitant, the mercury in the filtrate was further reduced to 4.8, 1.5, and 0.6 ppt, respectively. The improvement after adding precipitant resulted in an additional Hg reduction of 79, 52, and 67%, respectively. It is remarkable that the precipitant was able to form solids even with Hg concentration as low as < 2 ppt, resulting a filter Hg concentration of 0.6 ppt.

It should be noted that data column "A" indicates again "dissolved" mercury, which can be converted by adapting the REDOX potential (e.g. NaOCL dosing), and then filtered out, which may make dosing of polymers not required.

Microfiltration (MF) has been piloted as "feasible" technology as the "end of pipe" solution in the refineries/power plants (FGD) for very challenging feed streams. The last example is a pilot test using Pall Aria microfiltration pilot unit, similar to that illustrated in Fig. 8, with proved performance over a significant period of time.

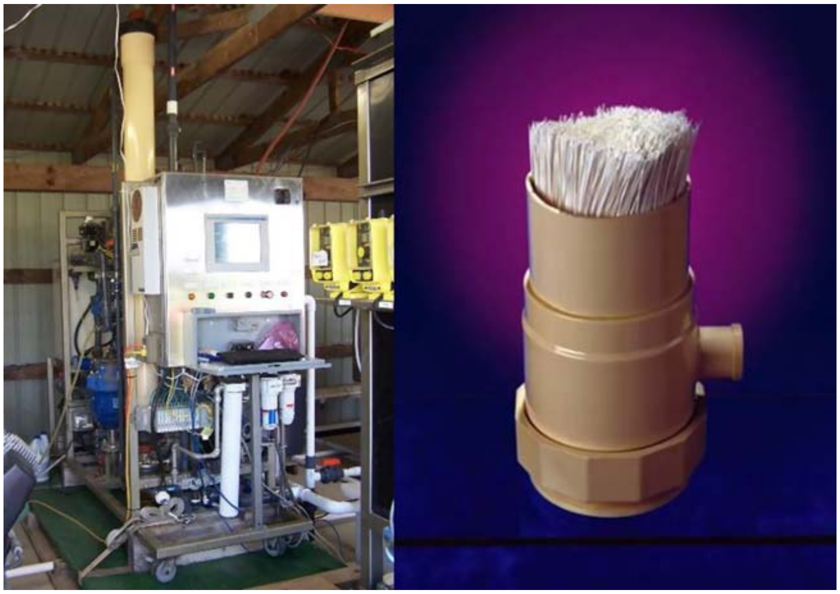

Fig. 8. Pall Aria pilot unit (left) with high-crystalline PVDF hollow fiber membrane modules (the module cutaway on the right).

The performance of Hg removal in refinery wastewater over a 16-month period with a Pall Aria microfiltration pilot unit is illustrated in Fig. 9. The feed water typically contained Hg concentration in a 20–40 ppt range. However, the feed Hg concentration might spike to tens of parts per billion (ppb) when upstream treatment processes encounter upsets. Fig. 9 indicates that the most filtrate samples showed a Hg concentration below 5 ppt when polyorganosulfide was not used, which is the regulatory discharge limit. The results demonstrated that microfiltration is a very robust process for Hg removal. Depending on the regulatory requirement, microfiltration by itself can potentially meet the regulatory requirement for Hg discharge. In the case where more stringent regulations apply or upstream process upsets occur, polyorganosulfide can be added to further lower the Hg concentration in the effluent. Besides excellent removal for Hg, the filtrate quality of microfiltration is high and consistent, which can lead the reuse of water for RO feed to produce boiler make-up or other process water for in-plant use.

4. Summary

As increasingly stringent environmental regulations for mercury apply, energy industry faces the challenge to lower mercury in wastewater discharge to the level of ng/L (ppt). It is difficult for conventional wastewater treatment systems to achieve such a low level of mercury in the treated effluent. Low-pressure membranes, applied directly or in conjunction with recently developed polyorganosulfide to form an insoluble complex with Hg, provide an alternative treatment technology for achieving Hg removal at the level of ng/L.

Microfiltration (MF) is to be used as the "end of pipe" solution in the refineries/power plants (FGD), for these very challenging feeds. Pall Aria™[1] Systems containing highly-crystalline PVDF microfiltration membranes with outstanding operating robustness not only provide a superior solution for Hg removal but also lead to the possibility of reuse of the wastewater. This will certainly reduce the water usage of refineries and power plants that have a large water footprint, or solving discharge problems with regard to mercury or turbidity.

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