Flotation, Filtration, and Adsorption: Pilot Trials for Oilfield Produced-Water Treatment

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Summary

As an oil field matures, it produces larger quantities of produced water. Appropriate treatment levels and technologies depend on a number of factors, such as disposal methods or usage aims, environmental impacts, and economics.

In this study, a pilot plant with a capacity of 50 m^3/d was used to conduct flotation, filtration, and adsorption trials for produced-water treatment at a crude-oil gathering facility. The flexible design of the plant allows for the testing of different combinations of these processes on the basis of the requirements of the water to be treated. The subject water during this study was a complex and changing mixture of brine and oil from different oil fields.

Induced-gas-flotation (IGF) trials were conducted, with different coagulant [polyaluminum chloride (PAC)] -addition rates from 0 to 820 $mg \cdot L^{-1}$. Inlet-dispersed oil-in-water (OIW) concentrations were quite varied during the trials, ranging from 39 to 279 $mg \cdot L^{-1}$ (fluorescence-analysis method). Turbidity also varied, ranging from 85 to 279 FTU. Through coagulation/flocculation and flotation, dispersed oils were removed from the water. PAC addition ranging from 60 to 185 $mg \cdot L^{-1}$ resulted in the reduction of the dispersed-oil concentration to less than 50 $mg \cdot L^{-1}$ in treated water; and PAC addition ranging from 101 to 200 $mg \cdot L^{-1}$ resulted in the reduction of the dispersed-oil concentration to less than 15 $mg \cdot L^{-1}$ in treated water. Turbidity was also reduced through flotation, with trial average reductions ranging from 57 to 78%. Filtration further reduced turbidity at rates greater than 80% through the removal of any suspended solids remaining from flotation. Activated-carbon adsorption reduced OIW concentrations of flotation-/filtration-treated water to 5 $mg \cdot L^{-1}$ (infrared-analysis method) through the removal of dissolved oil remaining in the water. Results confirmed that such adsorption treatment would be more practical for water with lower chemical-oxygen-demand (COD) concentration because high-COD concentrations in water reduce the lifetime of activated carbon dramatically.

Introduction

Oilfield-produced water is a byproduct associated with production of oil and gas. Most produced water requires treatment because it contains traces of dispersed and dissolved oil, heavy metals, boron, corrosive fluids such as H_2S and CO_2, production chemicals, radioactive isotopes, formation minerals, and other solids (Khatib and Verbeek 2002; Al-Manhal 2003; Fakhru'l-Razi et al. 2009). It is also very salty and, in some cases, is saltier than seawater. The treatment and disposal of produced water is a significant operating expense for oil and gas companies.

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In Oman, Petroleum Development Oman (PDO), the major oil-producing company in the country, typically produces approximately 8 m^3 water/m^3 oil for a total of 4.5 million BWPD (Al-Manhal 2009). Disposal or treatment methods depend on the intended use of the treated water. A large portion of produced water in Oman is treated and reinjected into the oil reservoirs to help maintain reservoir pressure, or it is used to generate steam for enhanced-oil-recovery (EOR) projects. Most of the remaining produced water is injected into deep-lying aquifers. This method of deepwater disposal is safe for the environment because the produced water is trapped well away from shallow aquifers used for drinking or irrigation. However, such deep disposal is expensive to operate because of the high levels of pressure needed to pump the water to its underground destination. The aquifers also have limited absorption capacity (Al-Manhal 2010).

PDO has been exploring environmentally acceptable alternatives for produced water. Pumping into the sea is uneconomic, given the high transportation costs involved in moving water to the coast. Pumping into exploitable shallow aquifers is ruled out because of the polluting effect on these potential future-water-supply sources (Al-Manhal 2009). In the case of low-salinity brines (up to one-sixth the salinity of seawater), the company is using reed plants to treat produced water (Al-Manhal 2010). Pilot hydrocyclones and gas-flotation projects are being executed with encouraging results (Al-Manhal 2009).

The choice of suitable methods/technologies is based on different factors, such as the characteristics and chemistry of the particular water; the target treatment level on the basis of reuse and discharge plans of treated water; the capital (equipment) and operating (power, chemical) costs; facility requirements (space)/treatment-unit mobility; durability/ease of operation and maintenance; and the requirement of pre- or post-treatment technologies/waste-stream byproducts (Arthur et al. 2005). The amount of dissolved and dispersed oil present in the produced water is related to oil composition, pH, salinity, total dissolved solids, temperature, oil/water ratio, type and quantity of oilfield chemicals, and type and quantity of various stability compounds such as waxes and asphaltenes. There is no single technology suitable for all effluent characteristics.

Many separate and combined physical, chemical, and biological methods are proposed for produced-water treatment. Available produced-water-treatment technologies (primary, secondary, and tertiary treatments) have been discussed in the literature with comparative evaluation (Kenawy and Kandil 1998; Plebon 2004; Arthur et al. 2005; Fakhru'l-Razi et al. 2009; Perry et al. 2009). Primary-treatment technologies include skim tanks, American Petroleum Institute oil/water separators, and various plate-pack interceptors, all of which target free oil and coarse solids (large droplets/particles >150 μm). Secondary-treatment technologies include flotation (e.g., dissolved gas, induced gas), flotation with coagulation (e.g., Al and Fe salt, polymer), hydrocyclones, and centrifuges, all of which target dispersed oil and fine solids (small droplets/par-

ticles between 20 and 150 μm) and generally reduce dispersed-oil concentration to <40 mg·L^{-1}. Hydrocyclones have been reported to be able to handle finer solids (5 to 15 μm), reducing oil and grease levels to 10 mg·L^{-1}. Polishing- and tertiary-treatment technologies include media filters (e.g., walnut shell, sand, anthracite), cartridge filters, membranes, adsorption (e.g., activated carbon), and biological treatment, all of which target emulsified oil and finer solids (smaller droplets/particles between 5 and 20 μm) and dissolved oil (droplets <5 μm) and reduce dispersed-oil concentration to <5–10 mg·L^{-1} (SPE 2011). A combination of more than one technology might be used in series operation.

While general data are available for the results of various treatment technologies, there is a lack of specific operational details concerning coagulant-addition rates for flotation. In this paper, trial treatment of oilfield produced water by use of a combined coagulation/flocculation, flotation, filtration, and adsorption treatment system is presented. A compact and mobile pilot plant of 50 m^3/d capacity was designed and fabricated on the basis of such chemical and mechanical treatment of produced water. The plant design allowed for the testing of different combinations of these processes to treat water to different levels of oil concentration, depending on need. For example, depending on the characteristics of the waste water to be treated for marine disposal, the secondary-treatment processes of coagulation, flocculation, and flotation alone may be sufficient. For use of the waste water for irrigation, additional tertiary-treatment processes of filtration and adsorption may also be required. The aim of trial operation of the pilot unit was to assist in the identification of suitable full-scale technologies that can be used to handle the huge quantities of produced water in Oman. In particular, flotation with PAC coagulant and adsorption by activated carbon are two techniques that, to the authors' best knowledge, have not been tested with produced water in Oman.

Experimental

Pilot-Plant Design. The pilot-plant system was designed with flexibility to be able to treat water to different levels according to need. The system combines different treatment processes, as follows:

- Coagulation/flocculation
- Flotation
- Filtration
- Adsorption

Coagulation/flocculation was selected as a pretreatment to flotation to agglomerate small oil droplets and suspended solids into larger contaminant floccules (flocs) to allow for more-efficient separation of contaminants from water and, consequently, smaller processing vessels. While the pilot plant can be used to test a variety of coagulants/flocculants, a combination of PAC and medium-strength anionic polymer (polyacrylamide, Takifloc A-103T) was used for these trials on the basis of bench-scale tests that also included consideration of ferric chloride ($FeCl_3$). PAC was selected over $FeCl_3$ because PAC use does not require pH control (PAC coagulation occurs in nearly neutral conditions), while $FeCl_3$ use would require pH neutralization as a result of pH drop during $FeCl_3$ coagulation. Additionally, water treated with PAC is clear, while color remains in water treated with $FeCl_3$ with incomplete coagulation. PAC is commonly used for wastewater treatment. The charged molecules in PAC enable ionic attraction among small oil droplets and fine suspended solids, resulting in an increase in particle size, which allows for easier separation. Polymer was added to further enlarge the contaminant flocs created by the addition of PAC and to allow for further improvement of rising velocity during flotation, resulting in a shorter residence-time requirement (i.e., smaller flotation-vessel size).

IGF was selected as an enhanced gravity-separation secondary-treatment technique, with microbubbles to help separate/lift contaminants to the water surface for removal. Flotation was selected because of its lower cost relative to other secondary techniques, and IGF was selected over dissolved-air flotation because of its ease in operation, minimal equipment requirements, and small footprint. N_2 was selected as the flotation gas for safety and maintenance issues related to corrosion and scaling.

Filtration was selected to remove any dispersed contaminants remaining in the water following flotation, and adsorption was selected to remove dissolved contaminants and any dispersed contaminants remaining in the water following filtration. While the pilot plant can be used to test a variety of filter media and adsorbents, sand and activated carbon were used during these trials because they were judged to be the most-cost-effective filtration and adsorption materials available.

Accordingly, the four main components of the plant are

- Mixing tanks, 2 units, volume: 0.5 m^3 each; operational capacity: 0.4 m^3 each
- Flotation tank, volume: 0.8 m^3; operational capacity: 0.63 m^3
- Filtration tower, volume: 0.5 m^3; operational capacity: 0.4 m^3
- Adsorption tower, volume: 0.5 m^3; operational capacity: 0.4 m^3

Additionally, there are holding tanks for raw water, scum, and treated water, and smaller chemical tanks for preparation and dosing of the chemical solutions required for coagulation and flocculation of water contaminants.

Different pumps convey water through the treatment processes and generate the microbubbles required for flotation. Mixers are used to prepare chemical solutions that coagulate and flocculate contaminants in the water. A scraper removes separated oily scum from the surface of the water in the flotation tank. A pressure-swing-adsorption (PSA) nitrogen generator supplies nonexplosive gas for flotation.

Basic-process and detailed pilot-plant-system flow diagrams are shown in **Fig. 1.** Raw water is collected from the pre-existing holding basin (T0) by the submersible holding-basin pump (E0) and supplied to the raw-water tank (T1). From there, the raw water is sent by the submersible raw-water pump (E1) to the mixing tanks (T2 and T3). PAC solution is dosed from the PAC tank (T10) by the PAC pump (E8) to the PAC mixing tank, where raw water and PAC are mixed to coagulate contaminants. There are provisions to add a second chemical if desired.

PAC-coagulated water flows to the pressure pump (E3) where nitrogen gas supplied from the PSA nitrogen generator (E4) is injected into the pump head to generate the microbubbles required for separation of contaminants by flotation. Polymer is dosed from the polymer tank (T11) by the polymer pump (E10) at the pump outlet to enlarge the flocs coagulated by PAC to allow for easier separation by flotation. A second pressure-pump system is available to increase system flow or as a spare.

From the pressure pump, coagulated/flocculated water enters the flotation tank (T4) where nitrogen microbubbles separate the chemical/contaminant flocs, carrying them to the surface from which they are removed by the scum scraper (E16) and then flow by gravity to the scum tank (T12). Water treated by flotation flows to the adjoining flotation-treated-water tank (T5).

Depending on the water level in the flotation-treated-water tank, the flotation-treated water is sent by filtration pump (E5) through the sand-filtration tower (T6) and the activated-carbon adsorption tower (T7) into the treated-water tank (T8). Valves and piping exist to bypass both the filtration and the adsorption towers or just the adsorption tower on the basis of the treatment processes being tested.

Additionally, for cleaning of the filtration tower and adsorption tower, there is a backwashing pump (E6).

Trial Sampling and Analysis. The Omani marine-disposal standard for "oil" in waste water in Oman is 15 mg·L^{-1} (Sultanate of Oman 2005). However, the method of analysis is not specified. Different analysis methods for oil concentration in water yield different results. As such, until the method of analysis is specified in

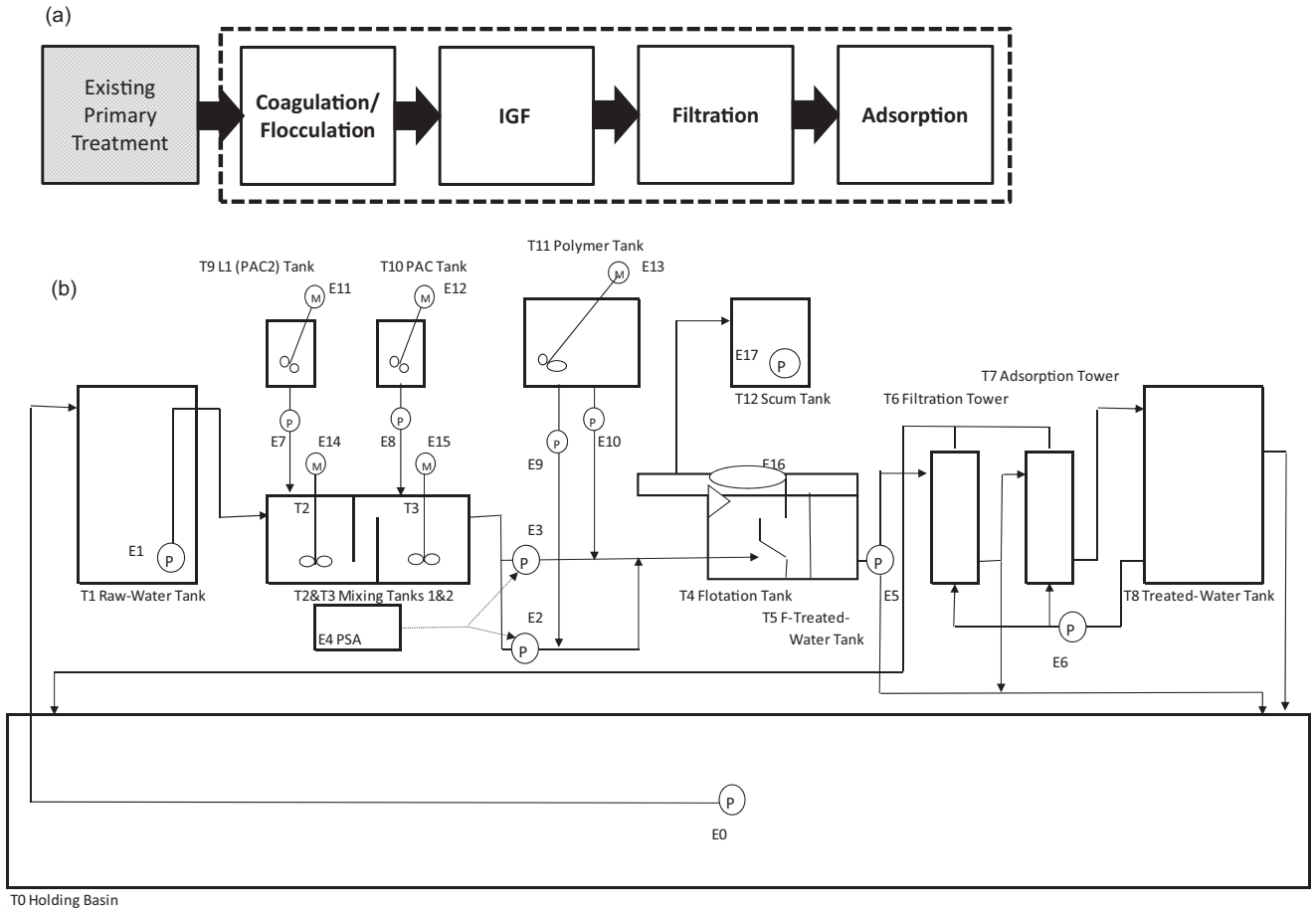

Fig. 1—Pilot-plant flow diagram (a) basic process and (b) detailed.

the Omani standard, some difficulty will remain in the selection of suitable oily-water-treatment processes for Oman.

During the trials, two different OIW-analysis methods were used: (1) for flotation trials, fluorescence analysis with a TD-500D OIW analyzer (from Turner Designs Hydrocarbon Instruments) was used because it analyzes dispersed OIW content, which is the target of the coagulation/flocculation/flotation process; and (2) for filtration/adsorption trials, infrared analysis with the InfraCal® TOG/TPH analyzer (from Wilks Enterprise Incorporated) was conducted because it is capable of analyzing dissolved-OIW content, which is the target of the adsorption process and is not analyzed by the TD-500D. The TD-500D analysis is a handy method that can provide quick results on-site and approximates the gravimetric method of oil and grease measurement [i.e., US Environmental Protection Agency Method 1664, the designated regulatory method in the US]. Similar to such gravimetric methods, the TD-500D does not effectively measure compounds such as benzyne, toluene, ethyl benzene, and xylene (BTEX), which may be dissolved in water. The TD-500D and such gravimetric methods measure the concentrations of less-volatile hydrocarbons that are more likely to be dispersed in water. The InfraCal® is capable of measuring compounds such as BTEX; thus, its results may present higher concentrations than results by the TD-500D, depending on the dissolved-oil content.

A single *n*-hexane (Hex) extraction method was used for the TD-500D analysis. InfraCal® analysis was conducted in conjunction with double tetrachloroethylene (TCE) extraction.

Where OIW-concentration and -removal-rate results are mentioned in this paper, they are followed by the method of measurement:

- TD-Hex (TD-500D with single Hex extraction)
- Inf (InfraCal® with double TCE extraction)

Turbidity was measured on-site with the Hanna® Instruments HI 93703 portable microprocessor turbidity meter (up to 1,000 FTU). COD was measured on-site with Kyoritsu COD Ion Selective Pack Tests WAK-COD (up to 100 $mg \cdot L^{-1}$) and WAK-COD(H) (up to 250 $mg \cdot L^{-1}$).

Depending on the trial, water samples were collected from up to four different points, as follows:

- Inlet (inlet to the pilot plant)
- Out GF (outlet from flotation/inlet to filtration)
- Out SF (outlet from filtration/inlet to adsorption)
- Out AC (outlet from adsorption)

Inlet-Water Characteristics. As mentioned earlier, crude oil is gathered at the trial site from many different oil fields. As such, water separated from such oil at the site is a complex mixture of different waters produced from different oil fields, posing a greater challenge compared with treatment of water produced from a single oil field. Furthermore, the characteristics of this mixture are continuously changing with time. **Fig. 2** shows the OIW concentration and the turbidity of inlet-water samples collected during the 6-month period of the flotation trials. OIW concentrations ranged from 39 to 279 $mg \cdot L^{-1}$ (TD-Hex) and turbidity ranged from 85 to 279 FTU.

Results and Discussion

Flotation Trials. Flotation trials were conducted over four different periods to identify a suitable coagulant (PAC) -addition rate.

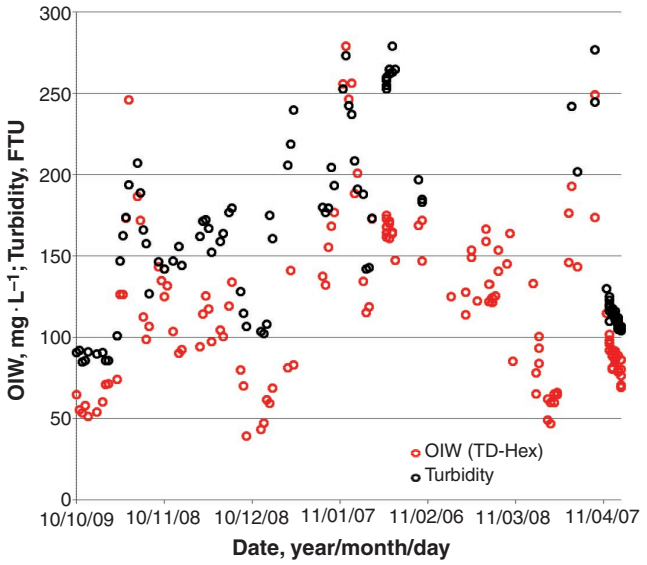

Fig. 2—OIW and turbidity of inlet water over time.

Because suitable PAC-addition rate depends on both inlet-water quality and treatment target, different inlet waters and treatment targets require different PAC-addition rates. Flotation Trial 1 was the initial testing period for examining the effect of different PAC-addition rates over a wide range of inlet-OIW concentrations. Results from this period were the basis for additional tests. Sludge-generation rates were also examined during this period. The second trial was conducted in a short period to minimize variation in inlet-water quality and to investigate the effect of PAC-addition rates for a narrower range of inlet-OIW concentrations. The effect of higher PAC-addition rates was studied during the third trial. For the fourth trial, variance in inlet-water quality was controlled by isolating the holding basin from which inlet water was collected, and the effects of polymer-addition rate and residence time were examined in addition to that of PAC-addition rate for a narrower range of inlet-OIW concentrations.

Flotation Trial 1. Different PAC-addition rates, ranging from 0 to 515 mg·L^{-1} with a 2 mg·L^{-1} polymer-addition rate, were tested over 4 months. Inlet and outlet samples were analyzed for OIW concentration by TD-Hex, and measured for turbidity. Additionally, the volumes of scum generated were also measured.

Inlet-OIW concentration varied greatly during the trial, ranging from 39 to 279 mg·L^{-1} (TD-Hex), as shown in **Fig. 3.** Inlet turbidity also varied greatly, ranging from 85 to 274 FTU, as shown in **Fig. 4.**

As explained in the introduction, PAC was added as a coagulant to increase contaminant size to allow for faster separation enhanced by flotation. Average flotation-outlet-OIW concentration for this trial period was 31 mg·L^{-1}. By comparison, these results were slightly better than those previously reported for established flotation processes (< 40 mg·L^{-1})

While maximum OIW removal and turbidity reduction were observed in the PAC-addition-rate range of 250 to 300 mg·L^{-1}, the optimal PAC-addition rate for OIW removal was 160 mg·L^{-1}, and the optimal rate for turbidity reduction was 150 mg·L^{-1} from analysis of the results. While OIW-removal and turbidity-reduction rates continued to improve after these optima, they were the rates from which gains in removal/reduction efficiency started to decrease with increasing PAC addition. At these optimal addition rates, OIW-removal rates were 85% (TD-Hex), and the turbidity-reduction rate was 55%. Where there was no PAC addition (i.e., 0 mg·L^{-1}), the OIW-removal rate (TD-Hex) was approximately 10%, and turbidity actually increased by approximately 10%. Some OIW is removed even without PAC addition, and this OIW is believed to comprise dispersed-oil droplets that were large enough to separate naturally by gravity in the given residence time without any size enhancement by coagulation/flocculation. The increase in turbidity is believed to be a result of the development of fine suspended solids caused by oxidation of such elements as S and Fe through exposure to air. Such suspended solids also require coagulant to allow for separation.

Scum generation increased with higher PAC-addition rates. At PAC-addition rates of 0 to 45 mg·L^{-1}, scum generation was approximately 1.5 vol%, as seen in **Fig. 5.** At rates of 90 to 200 mg·L^{-1}, scum generation increased to approximately 2 vol%. At rates greater than 250 mg·L^{-1}, scum generation further increased from approximately 3 vol% to a maximum of 3.2 vol% at 400 mg·L^{-1}. Scum increases with PAC addition because more contaminants are removed from the water with increasing PAC. Also, basically all PAC added to the treatment process is believed to be removed with the scum.

For the inlet-OIW concentrations observed during this trial, the minimum PAC-addition rate required to meet the Oman marine-disposal standard of 15 mg·L^{-1} was 147 mg·L^{-1} on the basis of the TD-Hex results. The minimum PAC-addition rate required to meet a lower target of 50 mg·L^{-1} was 60 mg·L^{-1} on the basis of the TD-Hex results.

Flotation Trial 2. The PAC-addition rate, with a 2 mg·L^{-1} polymer-addition rate, was increased from 0 to 350 mg·L^{-1} over

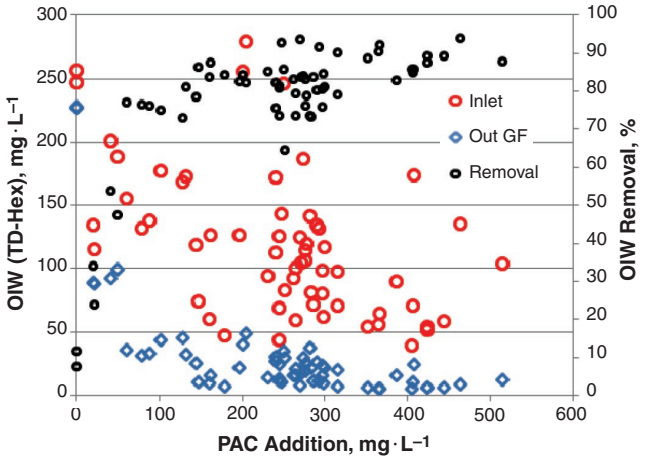

Fig. 3—Flotation Trial 1: inlet and outlet OIW and OIW removal vs. PAC addition.

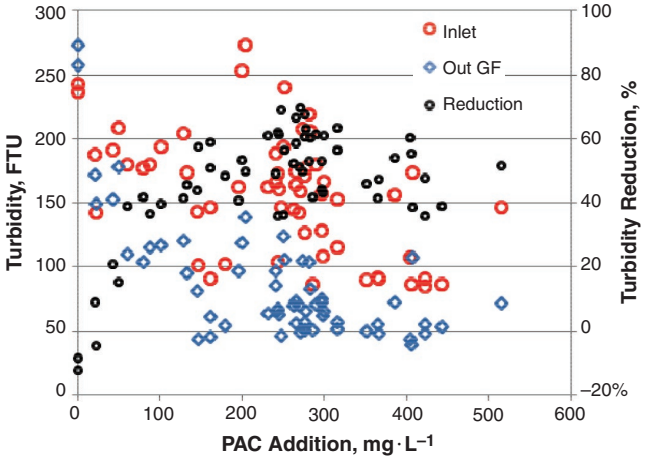

Fig. 4—Flotation Trial 1: inlet and outlet turbidity and turbidity reduction vs. PAC addition.

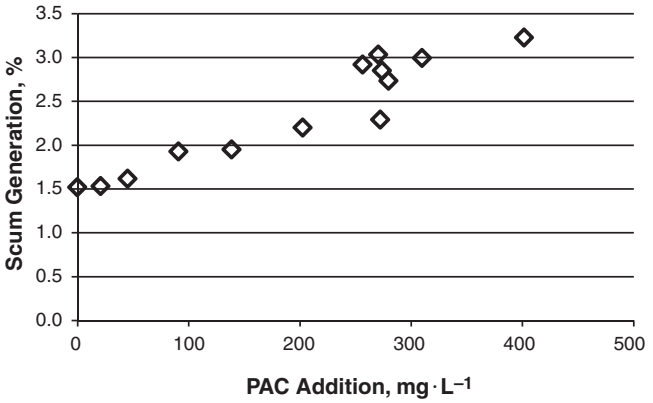

Fig. 5—Flotation Trial 1: scum generation vs. PAC addition.

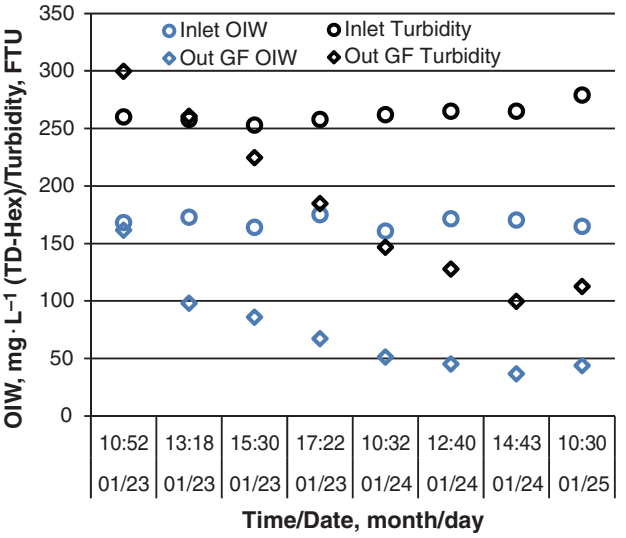

Fig. 6—Flotation Trial 2: inlet and outlet OIW and turbidity over time.

a short 3-day period of time in an effort to avoid a large variance in inlet-OIW concentrations and to limit the test to one variable of PAC-addition rate for a narrower range of inlet OIW. OIW was measured by TD-Hex, and turbidity was also measured.

The inlet-OIW concentration ranged between 161 and 175 mg·L^{-1} (TD-Hex), averaging 169 mg·L^{-1} (TD-Hex), as seen in **Fig. 6.** Outlet OIW was reduced as PAC addition was increased over time. A PAC-addition rate of 285 mg·L^{-1} with 78% OIW removal (TD-Hex) appeared to be the upper limit beyond which additional PAC did not result in any further removal, as seen in **Fig. 7.** This is similar to the result of Flotation Trial 1 in which the maximum OIW removal was observed in the PAC-addition-rate range of 250 to 300 mg·L^{-1}. The optimal value of Flotation Trial 2 is less obvious than the optimal value for Flotation Trial 1, but it appears to be higher than that for Flotation Trial 1. This is attributed to a higher average inlet-OIW concentration for Flotation Trial 2 because higher OIW concentrations generally require greater PAC addition. Without PAC addition (i.e., 0 mg·L^{-1}), the OIW (TD-Hex) -removal rate was 4%. Again, this was believed to be OIW comprising dispersed-oil droplets that were large enough to separate even without the use of coagulant.

Inlet turbidity ranged between 253 and 279 FTU, averaging 263 FTU, as seen in **Fig. 8.** Outlet turbidity was also reduced as PAC addition was increased over time. A PAC-addition rate of 285 mg·L^{-1} with 62% turbidity reduction appeared to be the upper limit beyond which additional PAC did not result in further reduction, as seen in Fig. 8. This is also similar to the result of Flotation Trial 1 in which maximum turbidity was observed in the PAC-addition-rate range of 250 to 300 mg·L^{-1}. Again, the optimal value of Flotation Trial 2 is less obvious than the optimal value for Flotation Trial 1, but it appears to be higher than that for Flotation Trial 1. This is attributed to higher average inlet turbidity for Flotation Trial 2 because higher turbidities generally require greater PAC addition. Without PAC addition (i.e., 0 mg·L^{-1}), turbidity actually increased by 15%. Again, the increase in turbidity is believed to be a result of the development of fine suspended solids caused by oxidation of such elements as S and Fe through exposure to air. Such suspended solids also require coagulant to allow for separation. Results for the inlet-OIW concentrations observed during this trial indicated that inlet water at this high range of OIW concentration [i.e., 161 to 175 mg·L^{-1} (TD-Hex)] could not be treated down to the marine-disposal standard of 15 mg·L^{-1} with flotation alone, as seen in Fig. 6. For the inlet-OIW concentrations observed during this trial, the PAC-addition rate required to meet the

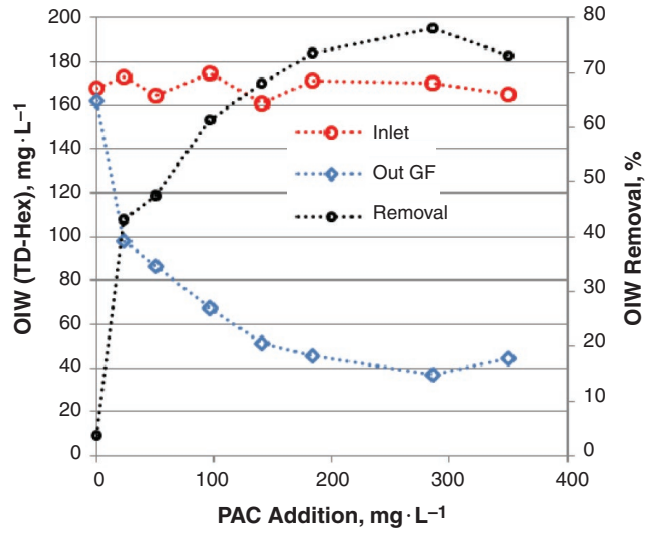

Fig. 7—Flotation Trial 2: inlet and outlet OIW and OIW removal vs. PAC addition.

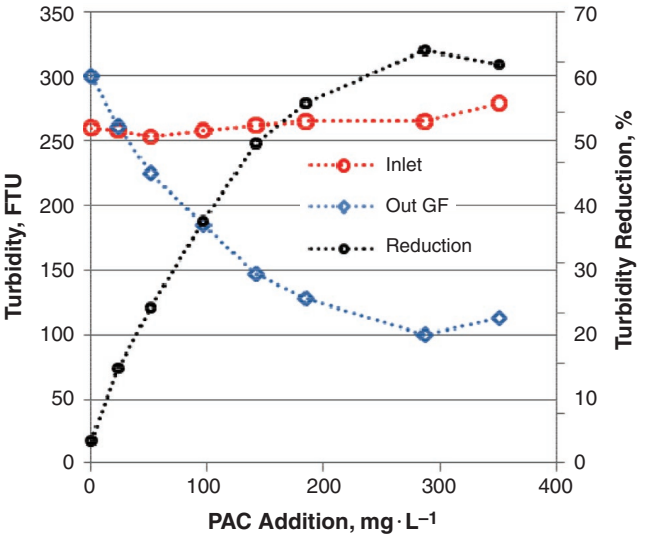

Fig. 8—Flotation Trial 2: inlet and outlet turbidity and turbidity reduction vs. PAC addition.

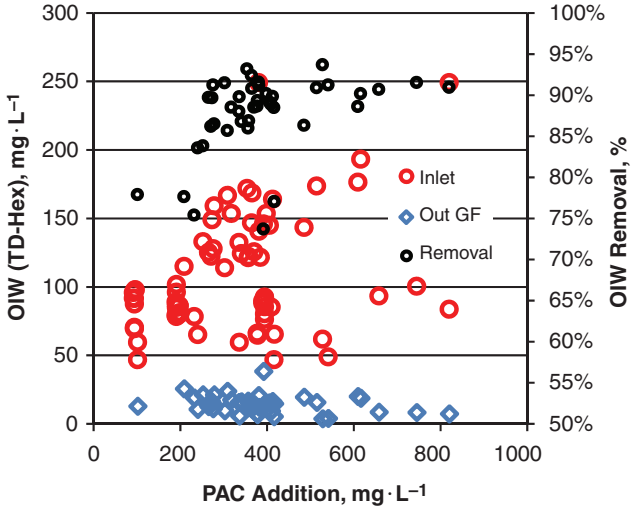

Fig. 9—Flotation Trial 3: inlet and outlet OIW and OIW removal vs. PAC addition.

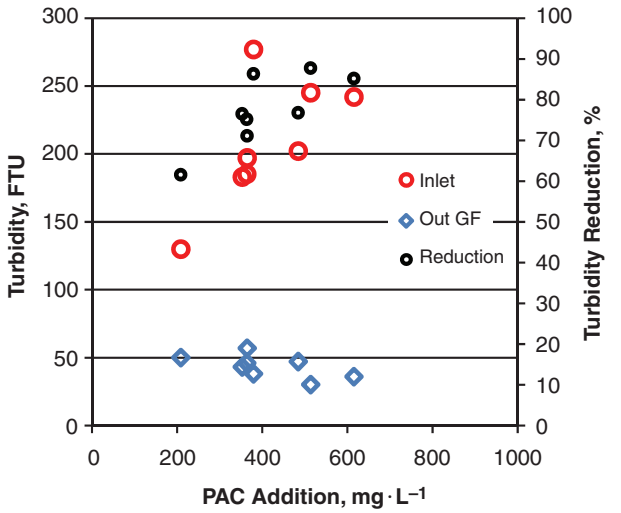

Fig. 10—Flotation Trial 3: inlet and outlet turbidity and turbidity reduction vs. PAC addition.

lower target of 50 mg·L^{-1} was in the range of 140 to 185 mg·L^{-1}—more than in the first trial period. While greater inlet-oil concentrations generally require increased coagulant addition, the exact reasons for elevated oil concentrations remaining in treated water are difficult to ascertain because of unknown variances in chemical constituents affecting treatment performance of water of different trials.

Flotation Trial 3. Higher PAC-addition rates, ranging from 101 to 820 mg·L^{-1} with varying polymer-addition rates ranging from 1 to 6 mg·L^{-1}, were tested. OIW was measured by TD-Hex, and turbidity was also measured for some samples.

There was great variance in inlet-OIW concentrations, ranging from 47 to 249 mg·L^{-1} (TD-Hex), averaging 122 mg·L^{-1} (TD-Hex), as seen in **Fig. 9.** Outlet OIW ranged from 4 to 38 mg·L^{-1} (TD-Hex), averaging 15 mg·L^{-1} (TD Hex). These results were better than those previously reported for established flotation processes (<40 mg·L^{-1}), were in the same range as those reported for hydrocyclones (>10 mg·L^{-1}), and even approached those for polishing and tertiary treatments (< 5 to 10 mg·L^{-1}), such as nutshell filters, activated-carbon adsorption, and biological treatment. OIW-removal rates ranged from 72 to 94% (TD-Hex) and averaged 87% (TD-Hex). The addition of PAC at rates greater than 400 mg·L^{-1}—at which the OIW-removal rate was 90% (TD-Hex)—did not appear to result in significant additional OIW removal.

The average outlet-OIW concentration was lower and OIW-removal rates were higher than in the first trial, while the average inlet-OIW concentration was basically the same. The better results were believed to be a result of the higher range of PAC-addition rates tested.

For the inlet-OIW concentrations observed during this trial, the minimum PAC-addition rate required to meet the Oman marine-disposal standard of 15 mg·L^{-1} was 101 mg·L^{-1} (the lower rate during this period) on the basis of TD-Hex results. The minimum PAC-addition rate required to meet a lower target of 50 mg·L^{-1} was, again, 101 mg·L^{-1} on the basis of TD-Hex results.

Inlet turbidity also varied greatly, ranging from 130 to 277 FTU and averaging 208 FTU, as seen in **Fig. 10.** Outlet turbidity ranged between 30 and 57 FTU, averaging 43 FTU. Reduction rates during the trial ranged from 62 to 88 FTU, averaging 78% turbidity reduction. The 400-mg·L^{-1} PAC addition, at which turbidity reduction was estimated at 70%, was seen as the optimal rate, after which increasing PAC-addition rate did not significantly improve turbidity reduction.

No changes to the OIW-removal rate were observed with the increasing polymer-addition rate.

Flotation Trial 4. To ensure minimal variance in inlet-water quality and better comparison of results, the holding basin was isolated. Different combinations of operational parameters were tested during this 1-week period. The operational parameters tested were as follows:

- PAC-addition rates: 100, 200, and 400 mg·L^{-1}
- Polymer-addition rates: 1, 2, and 4 mg·L^{-1}
- Residence times: 26, 32.5, and 40.5 minutes

Trial samples were analyzed for OIW, and turbidities were also measured.

There was a slight decline in OIW (TD-Hex) and turbidity over time, probably as a result of larger droplets of dispersed oil floating to the surface of the holding basin by natural gravity separation, while inlet water was taken from below the surface, as shown in **Fig. 11.** Nonetheless, variances were clearly less than during Flotation Trials 1 and 3, during which no such water-quality-control measures were used. Inlet-OIW concentrations ranged from 69 to 102 mg·L^{-1} (TD-Hex), and averaged 86 mg·L^{-1} (TD-Hex).

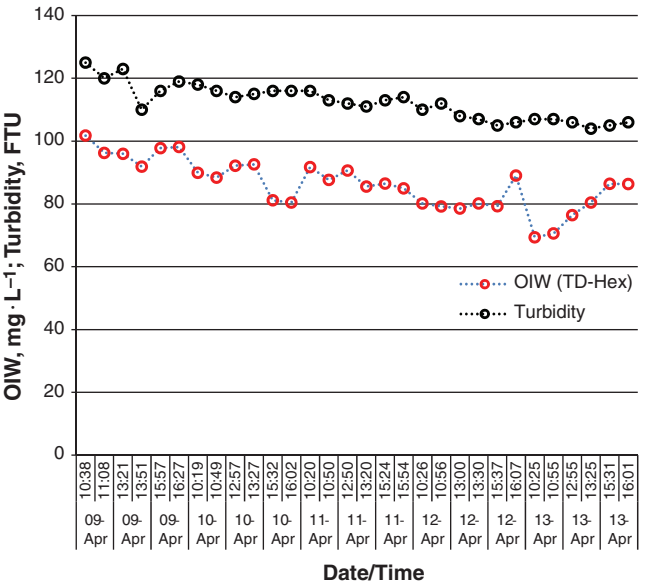

Fig. 11—Flotation Trial 4: inlet OIW and turbidity over time.

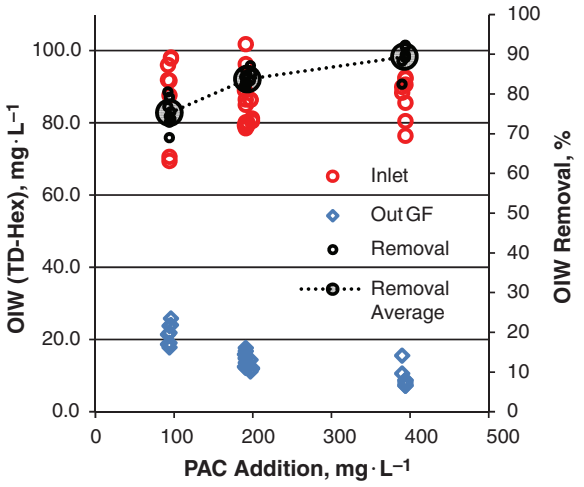

Fig. 12—Flotation Trial 4: inlet and outlet OIW and OIW removal vs. PAC addition.

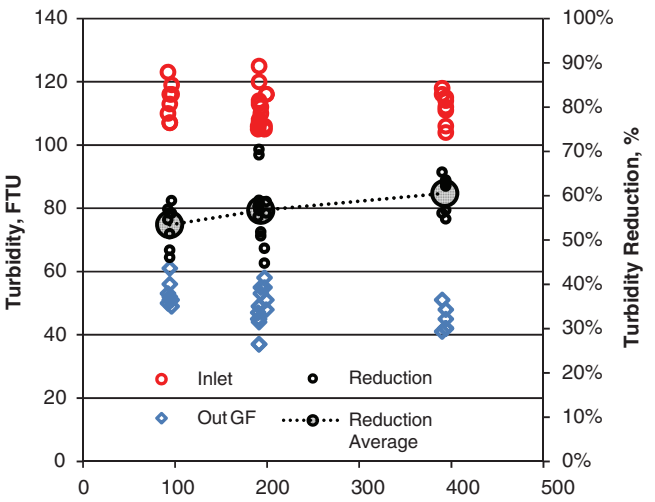

Fig. 13—Flotation Trial 4: inlet and outlet turbidity and turbidity reduction vs. PAC addition.

Outlet-OIW concentrations ranged from 7 to 26 mg·L^{-1} (TD-Hex), and averaged 15 mg·L^{-1} (TD-Hex), as seen in **Fig. 12.** Again, these results were better than those previously reported for established flotation processes (<40 mg·L^{-1}), were in the same range as those reported for hydrocyclones (>10 mg·L^{-1}), and even approached those for polishing and tertiary treatments (<5 to 10 mg·L^{-1}), such as nutshell filters, activated-carbon adsorption, and biological treatment.

With an increase in the PAC-addition rate from 100 to 200 mg·L^{-1}, the average OIW removal improved from 75 to 84% (TD-Hex). A further increase in PAC-addition rate to 400 mg·L^{-1} resulted in a less significant but additional 5% improvement to average OIW removal from 84 to 89% (TD-Hex). Of the three PAC-addition rates tested, 200 mg·L^{-1} appeared to be the optimal, with an average OIW removal of 84% (TD-Hex).

Inlet turbidity ranged between 104 and 125 FTU, averaging 112 FTU, as seen in **Fig. 13.** Outlet turbidity ranged between 37 and 61 FTU, averaging 48 FTU. Outlet turbidity trended slightly lower at higher PAC-addition rates, resulting in increased turbidity-reduction rates. At a 200 mg·L^{-1} PAC-addition rate, turbidity removal averaged 57%.

No significant effects were observed on either OIW or turbidity for the different polymer-addition rates and residence times tested.

Flotation Waste Reduction. The coagulation/flocculation and flotation processes result in the generation of oily scum, which is separated at the top of the flotation tank. Because this scum consists of mainly water (approximately 90%), significant reduction (97%) of waste volume can be achieved by separating water from the oily scum. As such, different dewatering devices available in the market were investigated, and one was selected as most suitable for the oily scum generated by the pilot plant. Compared with belt presses and centrifuges, the selected dewatering press is capable of handling scum with high water concentration without any prethickening. Additionally, the press does not require a storage tank, has a small footprint, consumes less power, requires minimal rinsing water, produces minimal noise and minimal vibration, is easier to maintain at lower cost, and is suitable for round-the-clock operation. Suitable polymer type and polymer-addition rates depend on the characteristics of the scum being treated, and were determined through beaker tests. Factors that determine the type and the amount of polymer include the presence of other chemicals in the water, contaminant concentration, and contaminant size. Scum-flow rate was then matched to polymer-solution concentration and dosing rate to determine optimal operational parameters for the selected dewatering press, as follows:

- Scum-flow rate: 0.5 m^3·h^{-1}
- Polymer-addition rate: 60 mg·L^{-1} (as powder)

The typical material balance for the scum generated by the pilot plant and treated by the dewatering press and sun drying was as follows **(Fig. 14):**

- 1 m^3 of water treated in the pilot plant results in 30 L of scum.
- 30 L of scum going into the dewatering press results in 3 kg of wet filter cake coming out of the press.
- 80% of the wet filter cake is water content.
- After sun drying, 3 kg of wet filter cake becomes 0.6 kg (750 mL) of dry cake.

Scum quality must be well monitored/managed for any changes because the dewatering press used is sensitive to such changes, which may result in clogging of the screw conveyor, thus requiring labor-intensive maintenance. Also, knocking out the air/gas in the scum, which results from flotation, is important (e.g., scum-settling tanks and/or mixers) before sending scum to the dewatering press because such air/gas affects performance. Additionally, a high-pressure washer was found to be useful for maintenance.

Flotation-Trials Summary. Four trials were completed in an effort to identify the optimal PAC-addition rate. Results of the trials are summarized in **Table 1.** Despite the complex mixture and continuously changing characteristics of the inlet water leading to

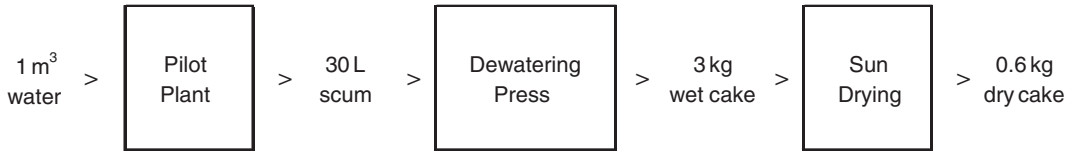

Fig. 14—Material balance for the scum generated by the pilot plant and treated by the dewatering press and sun drying.

TABLE 1—FLOTATION-TRIALS RESULTS SUMMARY

				Flotation Trial			
				1	2	3	4
PAC Addition			($mg \cdot L^{-1}$)	0–401	0–350	101–820	100–400
Minimum observed for		out < 15 $mg \cdot L^{-1}$	TD-Hex ($mg \cdot L^{-1}$)	147	*	101	200
		out < 50 $mg \cdot L^{-1}$	TD-Hex ($mg \cdot L^{-1}$)	60	140–185	101	100
OIW	TD-Hex	Range	Inlet ($mg \cdot L^{-1}$)	39–279	161–175	47–249	69–102
			Out GF ($mg \cdot L^{-1}$)	5–228	37–162	4–38	7–26
			Removal Rt (%)	8–94	4–78	72–94	69–92
		Average	Inlet ($mg \cdot L^{-1}$)	120	169	122	86
			Out GF ($mg \cdot L^{-1}$)	31	74	15	15
			Removal Rt (%)	77	56	87	83
Turbidity		Range	Inlet (FTU)	85–274	253–279	130–277	104–125
			Out GF (FTU)	38–273	100–300	30–57	37–61
			Removal Rt (%)	(–12)–70	(–15)–62	62–88	45–70
		Average	Inlet (FTU)	158	263	208	112
			Out GF (FTU)	86	182	43	48
			Removal Rt (%)	46	30	78	57
Scum Generation		at PAC 0–45 $mg \cdot L^{-1}$ (vol%)		1.5	**	**	**
		at PAC 90–200 $mg \cdot L^{-1}$ (vol%)		2.0	**	**	**
		at PAC 250 $mg \cdot L^{-1}$ (vol%)		3.0	**	**	**
		at PAC 400 $mg \cdot L^{-1}$ (vol%)		3.2	**	**	**

* not achieved
** not measured

some differences in the results between trials, the results showed that the system was capable of treating produced water of varying qualities effectively. The results indicated that the treatment was superior to that previously reported for established flotation processes (<40 $mg \cdot L^{-1}$), was in the same range as results reported for hydrocyclones (>10 $mg \cdot L^{-1}$), and even approached those for polishing and tertiary processes (<5 to 10 $mg \cdot L^{-1}$), such as nutshell filters, activated-carbon adsorption, and biological treatment.

Filtration/Adsorption Trial. Because of the high COD concentration in the inlet water, adsorption was expected to remove OIW effectively for only a relatively short period. The adsorption trial was carried out to confirm this. Because the target of this adsorption trial was dissolved oil remaining after the removal of most dispersed oil during flotation, OIW-measurement results from the Inf method were considered for discussion here because this method measures such dissolved oil while the TD method does not (OIW concentration of 22.4 $mg \cdot L^{-1}$ for Inf vs. 4.2 $mg \cdot L^{-1}$ for TD after flotation). Turbidity and COD were also measured on-site.

Flotation. Because this filtration/adsorption trial was conducted at a different time than previous flotation trials, inlet water for filtration was first prepared by pretreating by flotation. A PAC-addition rate of 300 $mg \cdot L^{-1}$ was used to ensure low-oil-concentration water for adsorption.

During the test, inlet-OIW concentration to flotation was initially unusually low, as seen in **Fig. 15.** Inlet OIW ranged from 25 to 112 $mg \cdot L^{-1}$ (Inf) and averaged 48 $mg \cdot L^{-1}$ (Inf). Inlet OIW increased after 200 hours as a result of the change in operation of upstream facilities, which affected the inlet-water supply to the pilot plant. Out GF OIW ranged from 17 to 39 $mg \cdot L^{-1}$ (Inf) and averaged 22 $mg \cdot L^{-1}$ (Inf). Flotation-OIW-removal rate was approximately 48% (Inf), as seen in Fig. 15. The lower removal rate is caused by inclusion in the analysis result of lighter hydrocarbon compounds (i.e., BTEX) that are detected by the Inf OIW-analysis method used during filtration/adsorption trials. Such compounds are believed to be dissolved in water and not removed by the flotation process and are not measured by the TD-500D OIW meter. As mentioned earlier in the Experimental section, because activated-carbon treatment targets dissolved hydrocarbons, the Inf method was used instead of the TD-Hex method, which was used during the flotation trials and targeted dispersed hydrocarbons.

Inlet turbidity ranging from 17 to 89 FTU and averaging 44 FTU was decreased to outlet turbidity ranging from 16 to 59 FTU and averaging 30 FTU. The average turbidity-reduction rate was 34%.

Filtration. Sand filtration was used after flotation to remove any remaining suspended solids from the water after flotation (i.e., to filter out any smaller flocs that may have leaked into flotation-

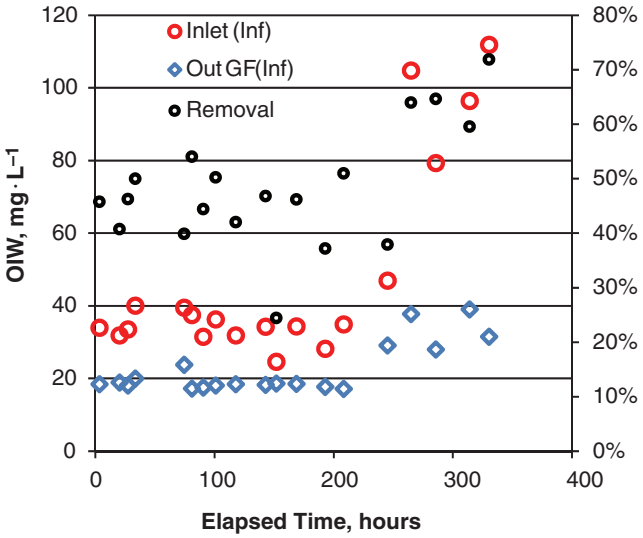

Fig. 15—Filtration/adsorption trial: flotation-inlet and -outlet OIW and OIW removal over time.

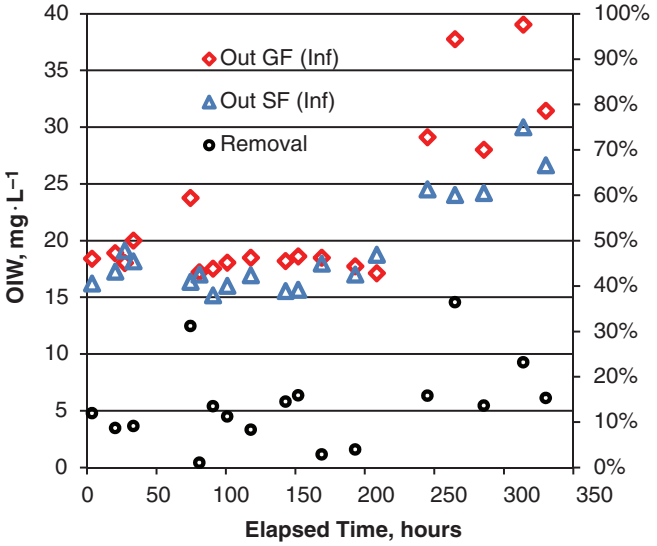

Fig. 16—Filtration-inlet and -outlet OIW over time.

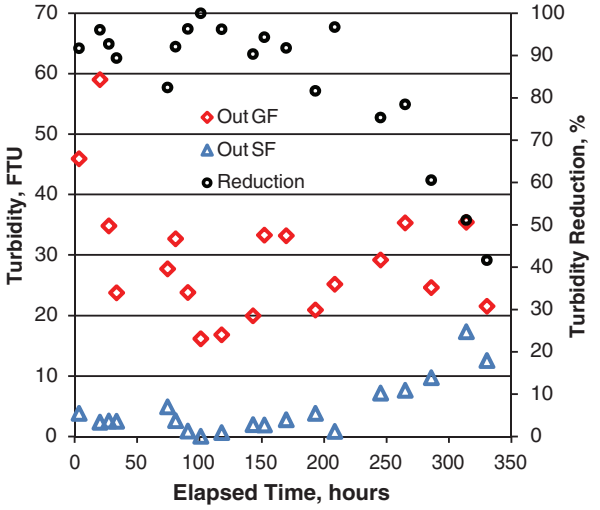

Fig. 17—Filtration-inlet and -outlet turbidity and turbidity reduction over time.

treated water because of insufficient residence time relative to floc size).

Significant OIW reduction from the filtration process was neither expected nor observed, as seen in **Fig. 16,** because most of the oil remaining in the water was believed to be dissolved. Out GF (filtration inlet) OIW was seen to increase after 200 hours because of the change in operation of upstream facilities carrying out flotation.

On the other hand, turbidity improvement was expected and clearly indicated because any remaining flocs were filtered out of the water. Filtration-inlet turbidity ranging from 16 to 59 FTU and averaging 30 FTU was reduced to filtration-outlet turbidity ranging from 0 to 17 FTU and averaging 4 FTU, representing an average reduction rate of 85%, as seen in **Fig. 17.** Again, after 200 hours, turbidity was seen to increase because of the change in operation of upstream facilities carrying through flotation and filtration.

Adsorption. As previously mentioned, because of the high COD concentration in the inlet water, adsorption was expected to effectively remove OIW for only a relatively short period. An adsorption test was carried out to confirm this.

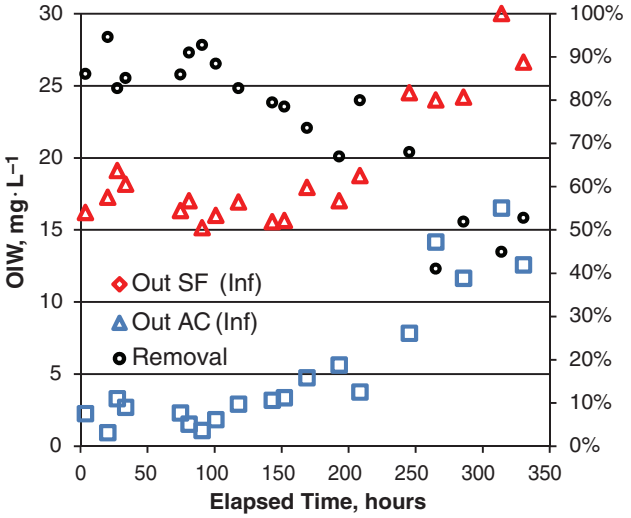

Fig. 18—Adsorption-inlet and -outlet OIW and OIW removal over time.

Activated carbon was selected as the test adsorption material because it is known for its treatment efficiency. Different types of activated carbons are available for a variety of purposes (i.e., adsorption of gas, solvent collection from gas, gas concentration/separation, odor removal from gas and liquids, color removal from liquids, dechlorination of liquids). For this trial, an appropriate commercial, granular activated carbon for highly efficient tertiary treatment of waste water was used because produced water is being considered for reuse for a variety of purposes, including those purposes requiring high-quality water. The characteristics of the activated carbon used in the adsorption test are as follows:

- Coal-based
- Density: 0.457 g/mL
- Grain size: 10:30 mesh (0.5–1.7 mm)
- BET (Brunauer-Emmett-Teller) surface area: 1200 m^2/g
- Iodine number: 1110 mg/g
- Methylene blue number: 200 mL/g

Inlet-to-adsorption OIW concentration ranged from 15 to 30 $mg \cdot L^{-1}$ (Inf) and averaged 19 $mg \cdot L^{-1}$ (Inf), increasing after 200 hours, as seen in **Fig. 18,** because of the change in operation of upstream facilities carrying out flotation and filtration.

Adsorption-outlet-OIW concentrations were initially less than 5 $mg \cdot L^{-1}$ (Inf) (Fig. 18), and the removal rate was approximately 90% (Inf). OIW concentrations began to increase and removal rate began to decrease at approximately 100 hours, exceeding the 15 $mg \cdot L^{-1}$ (Inf) threshold after 315 hours (Fig. 18), at which point the removal rate had decreased to approximately 50%.

The amount of OIW adsorbed was only (40–45 mg oil)/(g carbon), as seen in **Fig. 19,** probably as a result of the rapid saturation of the oil-adsorption capacity by high concentrations of nonoil COD. This is evidenced by on-site COD test results. Inlet-COD concentrations exceeding 150 to 250 $mg \cdot L^{-1}$ were reduced to less than 20 $mg \cdot L^{-1}$ for approximately 50 hours of operation, with removal rates exceeding 90%, as seen in **Fig. 20.** From 50 hours, the removal rate decreased, and, at 118 hours onwards, the activated carbon was no longer able to remove COD.

Filtration/Adsorption-Trial Summary. Dispersed oil and suspended solids are coagulated and flocculated during the initial stage of treatment. Most of the flocs containing oil and solids are separated out by flotation. Remaining flocs are removed by filtration, and some color and odor remain in the water. After adsorption, water becomes clear without odor. A summary of the OIW (Inf) results from the adsorption trial is shown in Table 2. Compounds

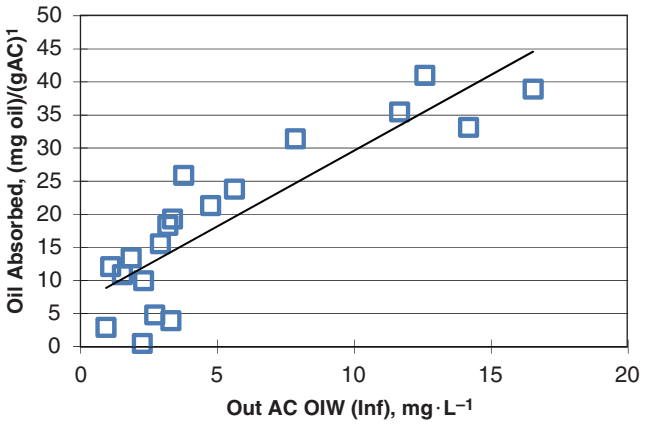

Fig. 19—Adsorption-trial activated-carbon isotherm.

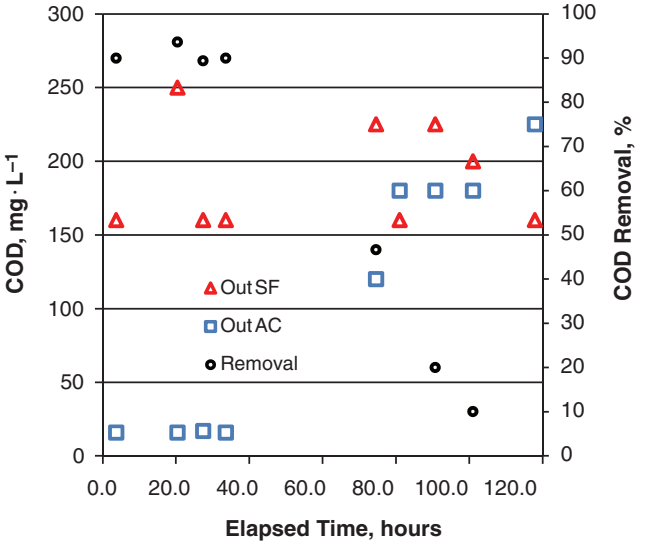

Fig. 20—Adsorption-inlet and -outlet COD and COD removal

dissolved in the water are not removed during flotation and filtration processes, and are subsequently removed during the adsorption process.

While activated-carbon adsorption works effectively to further reduce OIW concentrations well below the marine-disposal standard of 15 mg·L^{-1}, the high COD concentration of the waste water quickly saturates and dramatically shortens the lifetime of the activated carbon. Until a practical COD-pretreatment technique can be identified, activated-carbon adsorption, while effective, is not recommended for tertiary treatment of water with high COD concentrations in consideration of cost and maintenance. On the other hand, OIW (TD-500D) results after flotation are well below the Omani marine-disposal standard. As such, flotation alone may be sufficient without filtration and adsorption.

Conclusion

A summary of the results from the pilot-plant trial operation is as follows:

- IGF was effective in removing dispersed oil from the water with the addition of a PAC chemical. PAC-addition levels used during the trials were relatively high compared with what is expected to be necessary elsewhere (e.g., in the southern oil fields of Oman). However, while dispersed-oil concentrations varied greatly during the different flotation trials (i.e., averages ranging from 86 to 169 mg·L^{-1} with a PAC-addition level of 60 to 185 mg·L^{-1}), a dispersed-oil-concentration level of < 50 mg·L^{-1} was achieved. PAC-addition rates ranging from 101 to 200 mg·L^{-1} resulted in a reduction in dispersed-oil concentration to less than 15 mg·L^{-1} in treated water.
- Turbidity in water also varied greatly during the different flotation trials (i.e., averages ranging from 112 to 263 FTU). With PAC-addition rates greater than 100 mg·L^{-1}, turbidity-reduction rate averaged from 57 to 78% during the trials.
- Filtration further reduced turbidity in water from a range of 20 to 35 FTU to less than 10 FTU, translating to reduction rates greater than 80% in general.
- Activated-carbon adsorption was effective for the removal of oil remaining in the water after flotation and filtration. This remaining oil was believed to be mainly dissolved. Oil concentrations were reduced, on average, from 19 to 5 mg·L^{-1} during the adsorption trial. However, as expected, saturation of the adsorption capacity came early, owing to the high COD concentrations in the water at the time at this particular site. The use of activated carbon was confirmed to be more practical for sites with water with lower COD concentrations.
- The volume of waste generated by flotation was reduced successfully by 90% through the deployment of a dewatering press. The volume could be reduced further (by an additional 80%) by sun drying, resulting in a total volume reduction of 98%.

Acknowledgments

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