Concentrate Post-Treatment For Hydrogen Sulfide And Dissolved Oxygen

Vipin Pangasa, Laura Andrews, and William Green

The city of Venice hired Camp Dresser & McKee, Inc., to design an effective concentrate management system for its reverse osmosis water plant. Through CDM's assistance, the city obtained a permit from DEP for construction and operation of a new concentrate discharge line to the Venice Intracoastal Waterway. Currently the facility's RO plant concentrate is discharging into Hatchett Creek until the new discharge facilities are constructed and certified for operation.

The Venice RO water plant has been in operation since 1975. For design purposes, the city's RO plant is a 4-MGD facility using up to 8 MGD of feed water at an average recovery of 50%. The permit allows a maximum flow of 3.56 MGD during any consecutive 7-day average surface water discharge into the Venice Intracoastal Waterway. The anticipated maximum day concentrate flow will reach 4 MGD in the future.

Primary issues with the concentrate are the hydrogen sulfide and dissolved oxygen concentration levels. In accordance with the permit, the city must empirically maintain an H2S level below a maximum of 0.04 mg/L and a 30-day average of 0.02 mg/L and DO level at or above 5 mg/L in the discharged effluent. Based on historical data, the current total sulfides and DO levels in the untreated concentrate range between 1.5 - 2.5 mg/L and 3.0 - 4.0 mg/L, respectively.

An established effective means of removal or reduction of dissolved H2S from water or wastewater is through oxidation to elemental sulfur and then to sulfate. Oxidation may be achieved by several methods. The approach selected for the treatment of the Venice RO plant concentrate is through the addition of chlorine and injection of air combined with in-line static mixing. The addition of chlorine will facilitate the process of oxidation of sulfides present in the concentrate, whereas the air injection will raise the dissolved oxygen level of the treated concentrate discharge and potentially assist in the reduction of sulfides.

Objectives

To design the full-scale equipment for chlorine and air injection for concentrate treatment, CDM decided to run a pilot study on the plant effluent. The pilot study may not only help establish the efficacy of the proposed treatment but also, if effective, facilitate the selection of optimum dosage for both chlorine and air. In addition, the study may provide data to test the performance of in-line static mixers. Therefore, the objectives of the study may be listed as follows:

1. To determine the optimum dose of chlorine needed to reduce the sulfides present in the concentrate to below permitted compliance limits for discharge into the Venice Intracoastal Waterway (Class III waters).
2. To establish the interacting role of air addition, if any, in either reducing or facilitating the reduction of sulfides present in the concentrate and, thereby, establishing a reduced chlorine dosage.
3. To establish the quantity of air needed to raise the DO level of the concentrate to or above the permitted threshold (at or above 5 mg/L).
4. To establish the time and adequacy of the in-line mixing equipment in achieving the degree of homogenous mixing of the process reactants necessary to provide increased DO and reduced H2S.

Equipment Setup

The theoretical chlorine requirement for converting H2S to sulfate is 8.3 mg/L chlorine to 1 mg/L H2S. Chlorine usage concentrate treatment data from three similar RO facilities operating in Florida ranged from 1.3 to 6.1 mg/L per 1 mg/L H2S. To refine the chlorine requirements specific to the Venice RO facility concentrate, CDM, Koch-Glitsch (manufacturers of static-inline mixer equipment), and city staff worked together to conduct the pilot scale study.

A scaled down model of the proposed concentrate treatment system was constructed. Equipment and pipe sizing was based on the capability of the existing chlorine feed and air feed equipment to allow the pilot equipment to simulate the full scale scenario for the full range of chemical feeds expected.

A flow diagram is presented in Figure 1. A 2-inch PVC concentrate carrier pipe was used. Aqueous chlorine and compressed air were fed into the concentrate pipe. Sample taps (ports), flow meters, flow control valves, and pressure gages were included in the equipment.

The sample taps were placed to facilitate the sampling of the concentrate prior to any mixing : immediately downstream of chlorine feed but prior to chlorine inline static mixer (Sample Tap 2), downstream of chlorine mixer but upstream of air feed (Sample Tap 3), downstream of air feed and the primary absorber (gas-liquid mixer) but upstream of secondary absorber (Sample Tap 4) and downstream of secondary absorber and upstream of (final) free discharge into the existing basins (Sample Tap 5).

Vipin Pangasa, P.E., and Laura Andrews, P.E., are with Camp Dresser & McKee Inc. William Green is with the city of Venice.

Study Conditions

The pilot study was conducted between July and September 1999. To achieve the pilot study objectives, the following conditions were designed for sampling and analysis:

1. Chlorine solution was fed at differing dosage rates to the concentrate flow. Grab samples were collected from the five sample ports and analyzed for chlorine, total sulfide, DO, pH, and temperature.

2. Chlorine solution was fed at differing dosage rates along with air feed to the concentrate flow. Grab samples were collected and analyzed for chlorine, total sulfide, DO, pH, and temperature.

3. Concentrate flow was treated with different rates of air feed. Grab samples were taken and analyzed for total sulfide, DO, pH, and temperature.

Laboratory analysis calculates the unionized portion of the dissolved sulfide to enumerate the H2S concentration. However, dissolved hydrogen sulfide is quite volatile and readily escapes into the atmosphere. Therefore, determination of dissolved sulfide in the laboratory is subject to transportation losses, which result in lower values for hydrogen sulfide. To circumvent this, a preserved sample of the concentrate was analyzed for total sulfide. This analysis establishes a more stringent criteria for meeting the permit limits which, in turn, results in a need for a higher dose of chlorine to reduce total sulfides to permitted limits.

The concentrate flow rate was controlled using the concentrate flow control valve and the flow meter. The chlorine flow was controlled based on the rotameter settings and the chlorine flow control valve. The compressed air flow was also controlled using a flow control valve. During the study of the first two conditions (chlorine feed only and chlorine and air feed) the rotameter settings for the concentrate treatment were varied from 15 to 45 lbs/day. Since only a fraction of the actual plant concentrate flow was being utilized in this study, only a fraction of the chlorine thus fed was injected into the study concentrate. The range of rotameter settings provided sufficient chlorine feed range (fractional) to establish the optimum dosage on this pilot study. Chlorine was injected as aqueous

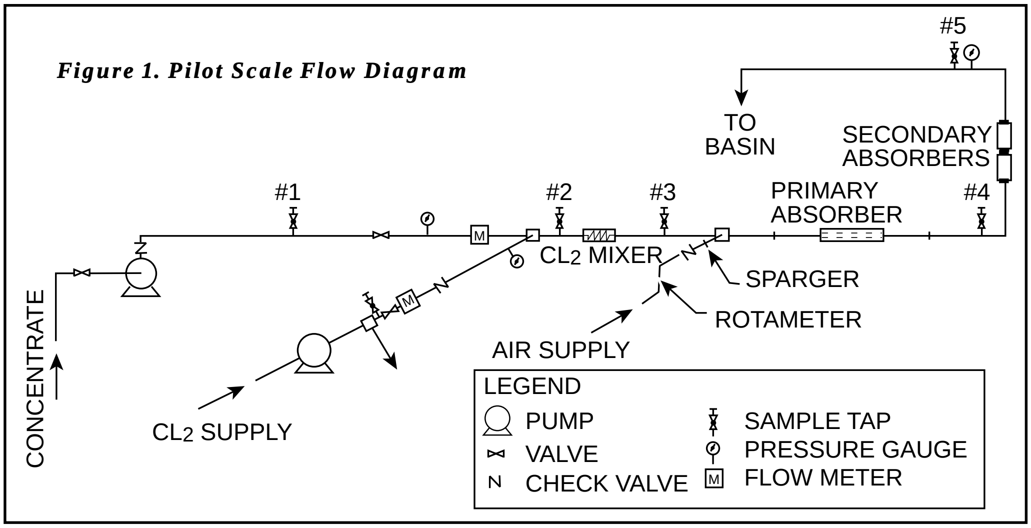


Figure 1. Pilot Scale Flow Diagram

chlorine using an in-line static mixer designed to achieve liquid-liquid mixing in a very short time. A static mixer unit with three elements was used for the mixing of aqueous chlorine with the concentrate. This mixer was placed in a horizontal orientation.

For the compressed air injection a multipoint injector (sparger) was used to facilitate air dispersion throughout the concentrate flow. For primary air absorption a mixer with seven elements was used in horizontal orientation. The secondary air absorber comprised two sets of mixers with three elements each. Both secondary absorbers (mixers) were installed in vertical orientation to enhance gas-liquid mixing. The air feed equipment allowed a feed range of 0-1.7 cubic feet per minute or 0-100 cubic feet per hour.

Results

The data collected during the pilot study is presented in Tables 1, 2, and 3. The Sample Tap 1 data helped establish the baseline parameter for the concentrate. The concentrate DO ranged between 3.1 and 4.4 mg/L, pH around 7.5, and total sulfides ranged between 2.0 and 2.2 mg/L. Once the base parameter concentrations were established (approximately), these data were not collected for rest of the feed settings.

Although residual chlorine quantities were not analyzed in the laboratory for the samples collected, a chlorine test kit was employed in the field to determine approximate chlorine concentrations to establish whether a reaction end point had been reached. In almost all cases the chlorine concentration reached 0 mg/L at Sample Tap 4, which indicated that all of the chlorine fed into the concentrate had reacted with the concentrate constituents. In the two cases where the chlorine test kit indicated a positive chlorine residual at Sample Tap 4, it also indicated the same amount at Sample Tap 5, thus suggesting that the reaction between chlorine and the concentrate constituents was essentially complete at Sample Tap 4. Because of this, and to provide a nominal degree of safety to the results obtained, the reduction of total sulfides to a concentration near zero was desired in the concentrate sample collected from Sample Tap 4.

Figures 2 and 3 plot the total sulfides concentration at Sample Tap 4 against

Table 1. Chlorine with Air Feed Pilot Data

			Sample Port 1			Sample Port 2			Sample Port 3			Sample Port 4			Sample Port 5		
Date	Air Flow (cfh)	Cl_2 Dose (mg/l)	DO	pH	Total S^{2-}	DO	pH	Total S^{2-}	DO	pH	Total S^{2-}	DO	pH	Total S^{2-}	DO	pH	Total S^{2-}
7/21/99	50 cfh	3.9	ND	7.42	2.02	ND	7.21	0.01	ND	7.36	0.96	ND	7.36	1.1	ND	7.35	1.04
7/21/99	50 cfh	7.0	3.5	7.46	2.1	3.41	7.08	0.01	3.52	7.29	0.32	4.73	7.34	0.52	4.57	7.34	0.47
7/21/99	50 cfh	9.3	3.65	7.48	2.12	3.07	6.92	0.01	3.09	7.2	0.01	4.86	7.28	0.04	4.79	7.26	0.06
7/21/99	50 cfh	12.8	3.53	7.44	2.16	3.6	6.92	0.01	3.64	7.16	0.01	4.68	7.25	0.01	4.73	7.2	0.01
7/22/99	50 cfh	11.6	3.5	7.49	2.06	2.87	6.97	0.01	3.15	7.17	0.01	4.53	7.27	0.01	4.91	7.24	0.01
7/22/99	50 cfh	8.5	3.05	7.45	2.08	3.08	7.02	0.01	3.28	7.21	0.01	4.67	7.35	0.18	4.67	7.3	0.18
7/22/99	50 cfh	5.9	4.02	7.5	2.02	3.47	7.16	0.01	3.19	7.32	0.38	4.69	7.4	0.5	4.82	7.34	0.57
7/26/99	60 cfh	2.9	ND	ND	ND	ND	ND	ND	3.46	7.4	1.43	4.73	7.47	1.44	4.66	7.46	1.62
7/26/99	60 cfh	7.6	ND	ND	ND	ND	ND	ND	3.8	7.34	0.38	4.57	7.39	0.44	5.82	7.37	0.46
7/26/99	60 cfh	9.8	ND	ND	ND	ND	ND	ND	3.72	7.33	0.22	4.6	7.41	0.35	4.69	7.35	0.32
7/26/99	60 cfh	10.9	ND	ND	ND	ND	ND	ND	3.3	7.3	0.28	4.65	7.38	0.24	5.02	7.31	0.16
8/10/99	60 cfh		12.0							2.73			5.08		0.01	5.53	
8/10/99	60 cfh		10.4							3.78			5.47		0.02	5.52	
8/10/99	60 cfh		9.4							3.81			5.2		0.15	5.11	
8/10/99	60 cfh		7.6							3.82			5.14		0.38	5.34	
8/10/99	60 cfh		5.8							3.74			5.11		0.66	5.09	

Table 2. Chlorine without Air Feed Pilot Data

			Sample Port 1			Sample Port 2			Sample Port 3			Sample Port 4			Sample Port 5		
Date	Air Flow (cfh)	Cl_2 Dose (mg/l)	DO	pH	Total S^{2-}	DO	pH	Total S^{2-}	DO	pH	Total S^{2-}	DO	pH	Total S^{2-}	DO	pH	Total S^{2-}
7/26/99	NA	5.0	3.37	7.51	ND	3.03	7.25	0.01	3.4	7.38	1.02	2.91	7.42	1.02	2.38	7.34	1.23
7/26/99	NA	6.9	3.79	7.51	2.22	3.41	7.14	0.01	3.64	7.34	0.9	2.79	7.34	0.72	2.49	7.34	1.02
7/26/99	NA	8.2	4.39	7.5	2.22	3.42	7	0.08	2.94	7.28	0.29	2.76	7.32	0.64	2.59	7.32	0.74
7/26/99	NA	9.5	3.7	7.54	2.18	3.6	7	0.11	3.56	7.32	0.25	3.39	7.3	0.35	2.52	7.27	0.47
8/10/99	NA	5.5							4.02			3.12		0.71	3.74		
8/10/99	NA	7.1							3.73			3.34		0.46	2.76		
8/10/99	NA	8.6							4.38			3.18		0.23	2.74		
8/10/99	NA	9.8							3.19			3.25		0.06	2.69		
8/10/99	NA	11.2							3.17			3.59		0.01	2.73		

NA = Not Applicable
ND = No Data (collected)

Table 3. Air Feed Only Pilot Data

Date	Air Flow		Concentrate		Sample Port 3		Sample Port 4		Sample Port 5	
	cfh	psi	gpm	psi	DO	Temp	DO	Temp	DO	Temp
9/1/99	27	24	42	12	3.19	26.9	3.68	26.9	3.9	27
9/1/99	50	24	41	13	2.56	27.1	4.18	27.2	4.15	26.9
9/1/99	75	24	40.5	14	3.3	26.9	4.41	27.1	4.36	26.9
9/1/99	98	25	40.5	14.6	3.25	26.8	4.28	26.9	4.36	26.8

the quantity of aqueous chlorine fed for two scenarios. The first scenario (Figure 2) plots the data obtained when both chlorine and air were fed to the concentrate and the second scenario (Figure 3) presents the data relationship obtained when only chlorine was injected into the concentrate stream. Since the stoichiometric relationship between chlorine and sulfide is linear (8.3 mg/L of chlorine per 1.0 mg/L of sulfide), a linear trendline was added to both figures.

A comparison of Figures 2 and 3 reveals two things. One, there is no significant reduction in the quantity of chlorine needed to reduce sulfides by injecting air into the concentrate stream; and second, the amount of chlorine needed to reduce sulfides to below significant levels (almost zero) appears to be between 11.0 and 11.25 mg/L. Having established the concentrate (influent) total sulfide concentration in the range of 2.0 - 2.2 mg/L, this would indicate that approximately 5.0 - 5.63 mg/L of chlorine is needed per 1 mg/L of total sulfide to reduce the sulfides to approximately zero. This dosage is lower than the 8.3 mg/L theoretical requirement but within the operating range of similar facilities.

As mentioned above, in almost all cases the chlorine concentration reached 0 mg/L at Sample Tap 4 indicating that all of the chlorine fed into the concentrate had reacted with the concentrate constituents and in the two cases where the chlorine test kit indicated a positive chlorine residual at Sample Tap 4, it also indicated the same amount at Sample Tap 5, thus, suggesting that the reaction between chlorine and the concentrate constituents was essentially complete at Sample Tap 4. This study data established the adequacy of the in-line static mixer (chlorine mixer) in achieving the degree of homogenous mixing of the process reactants necessary to provide sulfide reduction.

The data presented in Tables 1 and 3 indicate little increase (and sometimes even a decrease) in the dissolved oxygen level of the concentrate between sample ports 4 and 5. The one reading of 5.82 mg/L of DO at Sample Tap 5, indicating an over 25% increase, appears to be an anomaly. On the other hand, Tables 1 and 3, which present data corresponding to DO levels at Sample Taps 3 and 4, indicates a more consistent increase in DO concentrations - an average DO increase of approximately 1.4 mg/L. Based on the data interpretations made by the static mixer manufacturer, the performance of the primary absorbers in the case of combined chlorine and air is consistent with the theoretical expectations. The secondary air absorbers based on the data collected, however, do not meet theoretical expectations and may require a secondary air injection to improve the dissolved oxygen levels in the concentrate. For the air-only injection (Table 3) the DO levels are lower than theoretical expectations. Equipment limitations did not allow the air feed rate to be increased beyond approximately 1.7 cfm. The scope of the study also limited our ability to evaluate if other constituents present in the concentrate were reacting with oxygen.

Conclusions

1. The pilot study indicates that approximately 5.0 - 5.63 mg/L of chlorine is needed per 1.0 mg/L of total sulfide to reduce the latter to approximately zero.

2. Air feed plays an insignificant role in the reduction of total sulfides.

3. A secondary air injection system and/or the redesign of the secondary absorber is necessary to produce concentrate post-treatment DO levels consistent with the permit requirements (at or above 5 mg/L). Based on the performance of the primary absorbers and survey of similar facilities, it is estimated that approximately 4-5 cfm of air may be needed to produce a post treatment effluent with DO levels of 5 mg/L or more.

4. The static in-line (chlorine) mixer and the primary air absorber were found to function satisfactorily for mixing the process reactants and avoiding the need for significant detention times. The secondary air absorber, however, did not perform as expected. ■

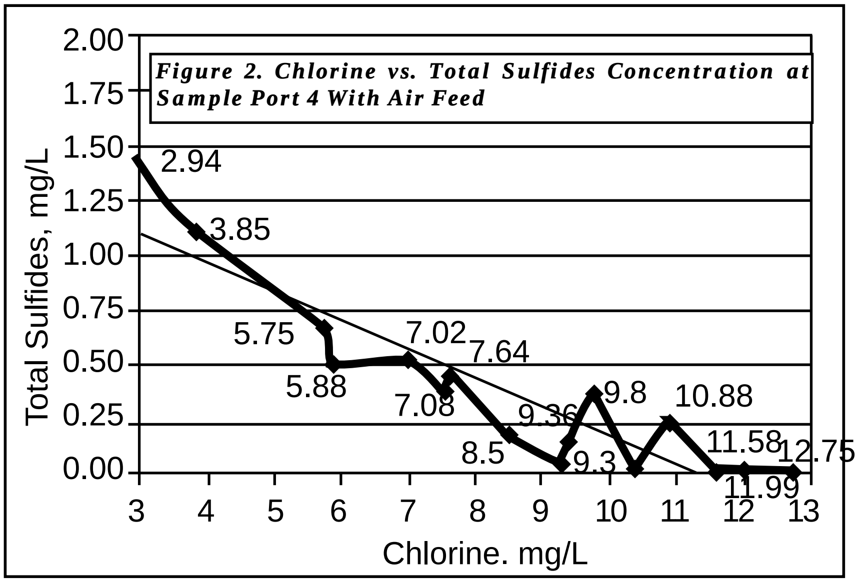


Figure 2. Chlorine vs. Total Sulfides Concentration at Sample Port 4 With Air Feed

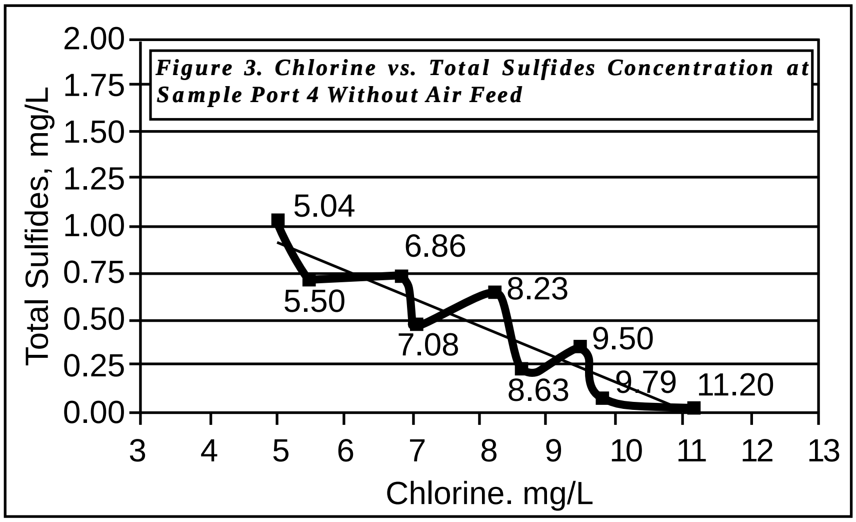


Figure 3. Chlorine vs. Total Sulfides Concentration at Sample Port 4 Without Air Feed

Recovering Spent Filter Backwash Water Using Dissolved Air Flotation Technology

Andrew Eades and Steve Scheidler

Andrew Eades and Steve Scheidler are with the F.B.Leopold Company, Inc., Zelienople, PA.

Recovering spent filter backwash water is currently receiving a great deal of attention. The issues are twofold: improving the net yield of a water treatment plant and reducing the risk of recycling pathogenic organisms in the backwash stream. Consisting of up to 10% of the total plant flow, spent filter backwash water is a considerable resource that should not be wasted. However, it contains materials removed by the filters — materials that may be inert, unstable, or even potentially pathogenic in nature, such as *Cryptosporidium* or *Giardia*. Regulators have recognized the need to understand the nature of the wash water in filter plants and are in the process of developing guidelines and regulations to help prevent the potential of a concentration loop developing in the backwash recycle.

Historically, simple equalization basins, and in many cases sedimentation lagoons, have been used from which supernatant is drawn off and pumped to the head of the treatment plant. While simple sedimentation does readily remove gross solids, smaller particles, which correspond to the more problematic Cryptosporidium *oocysts*, may not be removed in any great numbers without further chemical treatment.

Dissolved Air Flotation (DAF) is a system that replaces the sedimentation basins/lagoons with a process that introduces millions of micro-bubbles into the spent filter backwash water. The combination of bubbles and a small polymer dose, 0.2 – 0.3 mg/l being typical, forms a floc structure that floats to the surface of a tank. The sludge layer, removed using a mechanical skimmer, is typically 3 – 6% dry solids and has a small volume — approximately 0.1% of the incoming flow — much less than alternative technologies. Up to 99.3% of all solids is removed from the backwash water, and turbidities of < 1 NTU are routinely achievable. Influent turbidities of up to 600 NTU have been treated, with normal backwash water turbidities being 40 – 70 NTU. With the ability of removing the risk of recycling pathogenic organisms, DAF is an ideal system for meeting the challenges of the next set of EPA regulations. A simple schematic of a DAF system is illustrated in Figure 1.

This article discusses the results of a flotation jar test on one backwash water and a Leopold DAF pilot plant study on two others. Chemical addition to the backwash water was limited to polymer only, as it was quickly determined that coagulants were not needed in developing a particle structure suitable for removal by DAF. As primary coagulants were not used, there was no need to correct the pH of the system in operation, thus creating a very simple testing environment for both the jar tester and the pilot plant.

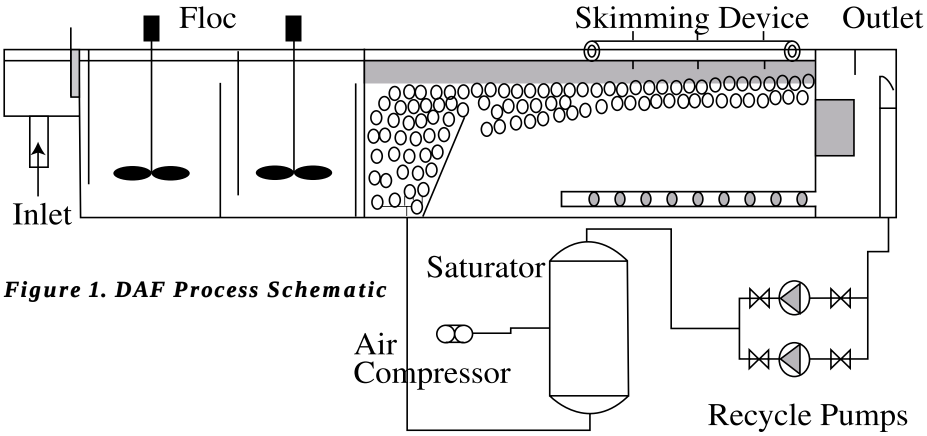


Figure 1. DAF Process Schematic

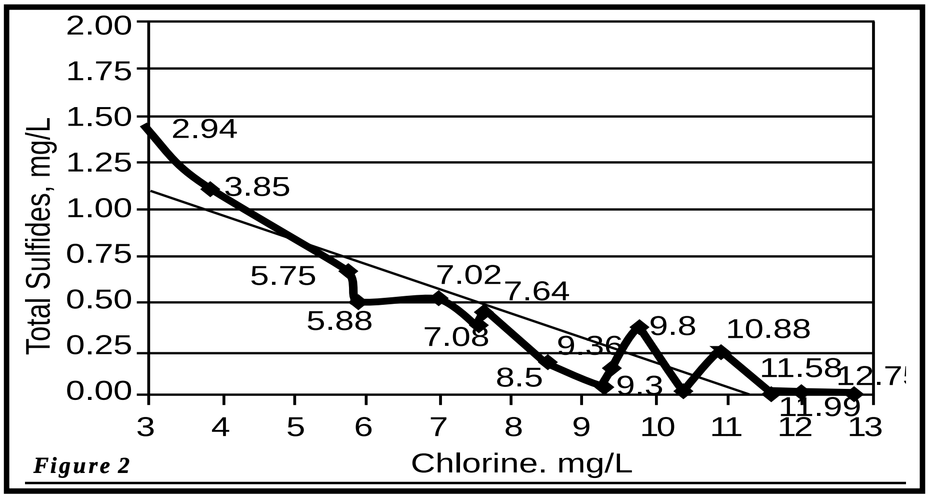


Figure 2

Jar Test Results

The jar test study was conducted on backwash water from a conventional sedimentation process followed by dual media rapid gravity filters. The backwash sequence uses surface agitators and a hydraulic only wash regime, creating a large amount of wash water but not with a high solids content or turbidity due to the higher wash volumes required for water only washing. Figure 2 illustrates a data set for the jar test study raw water turbidities and the DAF effluent turbidities. The groupings for the raw water reflect the spot sample nature of the analysis.

The results of the jar tests in removing this variable turbidity are given in Table 1. Clearly the DAF system is capable of treating this kind of backwash water with

Table 1. Statistical data set for DAF removal of NTU for full study period.

Data	Raw SFBW NTU	DAF Effluent NTU
Minimum	2.1	0.07
Average	11.9	0.52
Maximum	91	3.23

ease, but surprisingly it is also capable of producing waters that are well below < 1 NTU for the majority of the operational period, except where turbidities are approaching 100 NTU.

The excellent turbidity removals observed in the jar testing were achieved with only a required polymer dose of 0.1 – 0.2 mg/l of a cationic polymer. Using only a small polymer dose removed the need to use primary coagulants and hence pH correction.

The influence of polymer dose on the DAF jar tester performance can be seen in Figure 3.

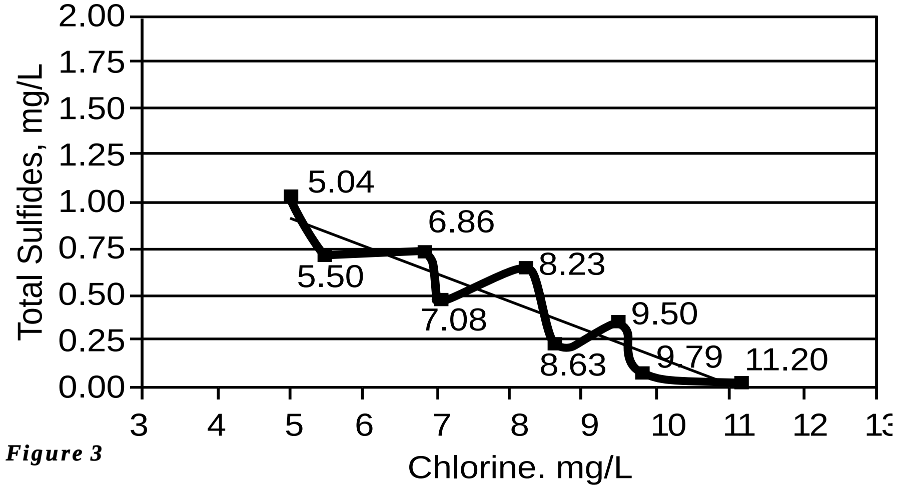


Figure 3

Pilot Plant Results.

The two pilot plant studies were of surface-stored water supplies and conventional water treatment systems in North Carolina and Colorado. In the North Carolina study the backwash water was treated directly by the DAF without prior settlement. In the Colorado study an existing backwash basin was used to determine the effect of pre-settlement on DAF performance.

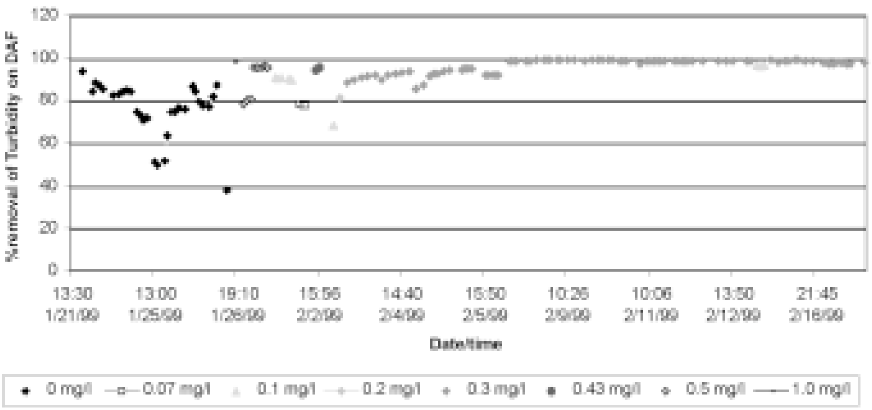
In the North Carolina study a problem with a sludge back feed in to the raw water holding tank created some very high turbidities that challenged the DAF system. The raw turbidity results are presented in Table 2.

Table 2. Backwash quality in North Carolina study.

SFBW batch number	Average NTU	Minimum NTU	Maximum NTU
1	583	377	730
2	56	34	72
3	36	35	39
4	165	152	182
5	72	70	74
6	385	379	390
7	160	146	176
8	54	47	75

The ability of the DAF system to treat this heavy turbidity water is evident in Figure 4.

Figure 4 Effect of Polymer Dose on DAF Performance



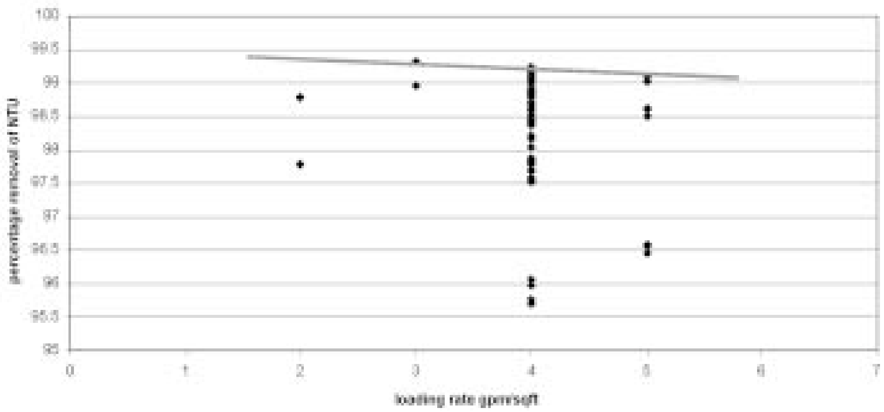
Turbidity removal rates were over 90% for almost all operational conditions tested, except where no chemical addition was undertaken. However, even with no polymer or primary coagulants the reduction in turbidity averaged over 75%, as shown in Table 3.

Table 3. Effect of polymer dose on pilot plant turbidity removal.

Polymer Dose mg/l	Raw NTU	DAF NTU	% rem on DAF	Polymer Type
0	578	143	76	LT22S
0.07	40	8.7	78	LT22S
0.1	61	8.5	85	LT22S
0.2	53	9.8	81	LT22S
0.3	114	2.1	97	LT22S
0.43	49	2.4	95	LT22S
0.5	58	5.5	90	Calgon 233
1.0	666	10	98	Calgon 233

The effect of loading rate on the DAF turbidity was also studied in detail at both sites. An important principle to understand with loading rate is that the residence time for the bubbles to "stick" to the polymer and floc is reduced with loading rate increase and thus is a very important design parameter. Figure 5 provides evidence that the DAF loading rate can be pushed hard, over 6 gpm/sqft under good chemical conditions and probably much harder. Given this, DAF proved to be a very compact and simple to operate system, having only a single polymer dose to control in a flow proportional manner and with a standard recycle rate of 10% of the incoming flow at design but operational at much less in a range of 5 – 8%.

Figure 5 Effect of Loading Rate on Percentage Removal of Turbidity



A benefit of DAF technology is the production of a low volume of high dry solids sludge. The sludge layer is produced out of the water and, as such, free drains before it is periodically removed to a collection system. Thus, the sludge is

Table 4. Typical sludge solids for a DAF system on backwash water.

Full Sludge Sample	%dry solids	Surface Sample	% dry solids
Average	4.83	Average	7.05
Minimum	3.1	Minimum	6.99
Maximum	5.1	Maximum	7.1
Sample Number	8	Sample Number	4

effectively thickened prior to removal, with typical solids as given in Table 4.

During the pilot plant trials the volume of sludge produced was monitored on a regular basis to understand how much sludge would need to be disposed of, a very expensive component of modern water treatment practice. It was found that sludge volumes ranged between 0.05 and 0.25% of the incoming flow. This can be compared to 1 – 5% for conventional sedimentation and sand ballasted flocculation, respectively, making the DAF system a significant improvement in backwash water treatment technology.

Conclusions

The studies demonstrated the suitability of DAF for low turbidity, pre-settled backwash water and for fully mixed higher solids flows, which are typically produced directly from the filter backwash launders.

The jar testing studies showed that zero flocculation contact time is a viable process choice for producing effluent turbidities in the range of the original raw water quality. The studies were verified at the pilot plant scale, on both heavy solids waters and on pre-settled water.

Primary coagulants were not needed to produce good effluent water quality. A small dose of a low molecular weight cationic polymer proved to be the only chemical addition needed in the system. The particles being treated are essentially stable, and polymer bridging, rather than hydroxide growth, seems to be the primary method of floc formation.

DAF process loading rates can be higher than typically used in potable water production. Up to 8 gpm/sq ft have produced satisfactory results. Recycle rates of 8-10% of the incoming flow volume were the same as for potable water production.

Sludge solids produced by the DAF system have been measured up to 7% dry solids. Such a high solids, low volume sludge stream can eliminate secondary thickening.

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