SPES Membranes

By Brandon Yallaly, Adam Zacheis & Bob McVicker

New NF plant treats high-color, low-TDS groundwater

Mesa Consolidated Water District (MCWD) was formed on Jan. 1, 1960, to manage and deliver water and water-related services to customers within its 18-sq-mile service area in Orange County, Calif.

In the late 1990s, MCWD constructed the Colored Water Treatment Facility (CWTF) for treatment of high-colored groundwater using ozone and biologically active carbon. In 2003, an additional bromate removal step was added in response to increasing levels of bromide in the groundwater.

Due to steadily increasing groundwater color and bromide levels, the district initiated the CWTF Technology Replacement and Expansion Project in 2010 to construct a state-of-the-art nanofiltration (NF) treatment plant for groundwater color removal. The new water treatment facility will utilize low-rejection sulfonated polyethersulfone (SPES) membranes, which have negative surface charges ideally suited to reject natural organic matter without fouling from organic adsorption. Pilot testing and design began in January 2010, and construction commenced a year later.

Water Quality

The design raw water quality and finished water quality goals are presented in Table 1. Because the selected NF membranes remove very little calcium and bicarbonate/carbonate ions, the resulting permeate is not overly aggressive when compared to traditional NF and reverse osmosis permeate.

Low raw water hardness and hydrogen sulfide (H_2S), however, make post-treatment challenging. Without alkalinity recovery and pH adjustment following H_2S removal, the NF permeate would be poorly buffered against changes in pH levels and corrosive to distribution system piping.

Table 1. Raw and Finished Water Quality

Parameter	Unit	Design Raw Water Quality	Finished Water Quality Goal
Alkalinity	mg/L as $CaCO_3$	200	>140
Sulfide	mg/L	Up to 0.95	>0.1
Hardness	mg/L as $CaCO_3$	32.0	>20
pH	pH units	8.8	8.5 to 9.0
TDS	mg/L	361	<500
Color	Color units	300	<5

NF System

The selected SPES membrane exhibits its poor rejection of ionic constituents but high levels of low-molecular-weight-cutoff compound rejection, which is ideally suited for the low total dissolved solids (TDS), highly colored CWTF well water. Because of the low salt rejection and low TDS feedwater, system recoveries of up to 98% are possible. To achieve recovery levels in this range, primary and secondary NF systems will be used.

The primary two-stage NF system with concentrate recycle allows for operation with up to 95% recovery. The SPES membrane displays a unique rejection property: As the feedwater TDS increases, the salt rejection decreases. This phenomenon allows recycling of the concentrate and presents a benefit for downstream post-treatment due to increased calcium concentration in the permeate. Additionally, a two-stage system with concentrate recycle has lower energy usage than a three-stage system (based on models calibrated against pilot data), which differs from traditional NF systems and is most likely due to the lower osmotic pressure that results from the reduced salt rejection.

The secondary NF system will utilize a single-stage array that allows for up to 67% recovery.

Hydrogen Sulfide & Methane Removal

The raw water contains some methane (less than 10 mg/L) and dissolved sulfide (ranging from 0.5 to 1 mg/L). Due to the pH level of the raw water (pH greater than 8.5), the sulfide exists almost exclusively as dissolved sulfide. In this form, sulfide oxidizes to sulfur when exposed to chlorine. Sulfide oxidation with sodium hypochlorite can cause turbidity issues due to sulfur formation, which was confirmed with jar testing.

Prior to the discovery of sulfide in the raw water, methane removal was to be accomplished using the fine-bubble diffuser and blower systems installed in the existing ozone contactor—a concept that also takes advantage of the hydraulics of the existing system. In an effort to avoid pH adjustment, air stripping and alkalinity recovery, the following chemical options were investigated to avoid the capital costs of decarbonators and pH-adjustment chemicals:

- Chloramination for oxidation of H_2S;
- Conventional oxidation of sulfide by free chlorine, chloramines, hydrogen peroxide or permanganate at the permeate pH range of 8.7 to 8.9;
- Aggressive oxidation with chlorine dioxide or ozone, as both are powerful enough to fully convert sulfide species to sulfate;
- Chlorine and sodium metabisulfite (SMBS), with SMBS added after chlorination of sulfide to remove colloidal sulfur, and a second step of chlorination for complete conversion of all sulfide species to sulfate; and
- Permeate stream pH adjustment to around 6.2 followed by chlorination.

These alternatives all had fatal flaws ranging from turbidity, chlorite, assimilable organic carbon or bromate formation to excessive chemical use and unacceptable TDS increases. Therefore, pH adjustment and countercurrent-forced air stripping for post-treatment is the selected method of H_2S and methane removal despite the lost hydraulic benefits of the existing ozone contactor.

The existing ozone contactor will be converted to a transfer pump station.

Alkalinity Recovery

Dissolved carbon dioxide (CO_2) is stripped readily from the NF permeate when passing through the degasifier. At pH below 6.3, the majority of the carbonate species in the water is in the CO_2 form and is stripped out with the H_2S. Therefore, carbonate must be added back to the finished water to provide the necessary alkalinity for pH stability and corrosion control, especially given the low calcium concentration in the raw water and NF permeate. To recover the lost alkalinity, carbonic acid is injected into the degasifier effluent after the addition of caustic soda and converts to bicarbonate alkalinity.

Residual Disinfection

Due to the bromide in the NF permeate, extended exposure to free chlorine was minimized to avoid bromamine formation. Chlorine and ammonia will be added in to the degasified permeate in close proximity to one another to prevent disinfection byproduct formation.

Pilot Testing

Results of the pilot test indicated no operational issues with a system recovery of 95% and a flux rate of 16 gal per square foot per day. Color removal was exceptional, with a reduction from 260 color units to 2 or 3 color units, with no indication of fouling or scaling. Color removal efficiency did not appear to be influenced by flux rate or recovery.

Feed pressures were stable, and preliminary data suggests that pressures are influenced almost exclusively by flux rate—not recovery—most likely because the SPES membranes do not reject salts well.

Summary

The application of SPES membranes for low-salinity, high-color groundwater will allow MCWD to maintain alternative water supply development despite changing raw water conditions. Additionally, the new CWTF, scheduled for completion in the spring of 2012, will simplify operations and allow the district to continue meeting customer needs for decades to come. MT

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