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FILMTEC Membranes

Water Chemistry and Pretreatment: Treatment of Feedwater Containing Hydrogen Sulfide

Treatment of Feedwater Containing Hydrogen Sulfide

Some well waters, usually brackish waters, are in a reduced state typically lack of oxygen (therefore referred to as anoxic or anaerobic) and the presence of iron, manganese, ammonium and/or hydrogen sulfide (H₂S). H₂S in ground water aquifers usually occurs at concentrations of 0.5 to 5 mg/L as the result of the dissolution of minerals in geologic deposits or as anaerobic bacterial activity on organic sulfur, elemental sulfur, sulfates and sulfites. The amount of sulfide dissolved in water is pH dependent as shown in the following equations:

$H_2S + H_2O = H_3O^+$	+ HS⁻	pK ₁ = 7.0
$HS^{-} + H_2O = H_3O^{+}$	+ S ²⁻	pK ₂ = 14.0

H₂S levels as low as 0.1 mg/l can adversely affect the performance of RO or NF systems.

Prevention of Potential Problems on Feed/Concentrate Side of Membrane

The presence of H_2S in feed water exposed to oxidants (e.g., oxygen in air, chlorine) can result in the precipitation of elemental sulfur or metallic sulfides. The deposits can have a black sooty appearance or be a gray pasty residue that clogs filter cartridges and coats the feedwater piping. Not only will these precipitated solids cause a higher than normal filter cartridge replacement rate but, because the particle size for metallic sulfides and colloidal sulfur is in the sub-micron range, a significant quantity of precipitants will pass through the typical 5 micron (μ m) rated filter cartridge. These suspended solids will accumulate in the feed/concentrate channel spacer of the RO or NF membrane elements, increasing the operating differential pressure. Further accumulation of sulfur and metallic sulfides on the membrane's surface will cause an increase in salt passage and a decrease in flux reducing the system efficiency.

Air can also be introduced into the feed/concentrate area in RO or NF elements as a result of siphoning in the concentrate piping. This is particularly likely when a long run of pipe is used for the concentrate line. A siphon breaker should be used to prevent creation of the partial vacuum that tends to draw water from the feed/concentrate side of the membrane again producing voids that can introduce air. Drain lines discharging directly to floor drains or trenches should be provided with a suitable air-gap to avoid contamination problems associated with "cross-connections". The use of spring-loaded check-valves in the concentrate line will also help prevent siphoning. The piping arrangement should be designed to keep the RO or NF membrane skid assembly "flooded" and free from air during idle periods.

Colloidal sulfur may be difficult to remove. A solution of sodium hydroxide (NaOH) with a chelating agent such as EDTA is an appropriate cleaner. If the foulant is not heavily composed of elemental sulfur, a phosphoric acidic solution may be capable of dissolving out the sulfide components. High velocity permeate flushes may also be beneficial. See <u>Cleaning Procedure (Section 6.5)</u> for cleaning procedures.

Treatment of Feedwater Containing Hydrogen Sulfide (cont.)

Prevention of Potential Problems on Permeate Side of the Membrane

Since H₂S is a gas, it passes through the membrane barrier layer and, under certain conditions, will precipitate as elemental sulfur in the membrane microporous polysulfone substrate, polyester supporting web and permeate channel spacer. An ivory to yellowish precipitate is formed on the "backside" on the membrane composite when H₂S is exposed to an oxidizing environment, such as on shutdown when air enters the permeate side of the system. There is a tendency for a reverse flow of water from the permeate side of the membrane to the feed/concentrate side as the result of natural osmosis. This is particularly significant in high salinity waters containing >6000 mg/l of total dissolved solids (TDS). This back-flow can introduce air into the permeate side of the membrane element. A freshwater flush is recommended, especially for feeds containing H₂S, to displace the concentrated solution as part of any shutdown sequence. This eliminates any osmotic driving force for back-flow. However, in locations that experience frequent losses of electrical power that lead to unscheduled shutdowns where flushing is not possible, a "suck-back" or "draw-back" reservoir located in the permeate piping elevated above the top pressure vessel is recommended. This draw-back tank should be of sufficient volume to makeup any back flow due to osmosis that occurs during an unscheduled shutdown - see Tanks (Section 3.13.6).

Sometimes a technique is used to prevent a negative transmembrane pressure (higher pressure on the permeate side than on the feed/concentrate side) greater than 5 psi (0.3 bar). This is commonly done using a dump valve to relieve pressure on the permeate line upon system shutdown. For systems with feeds containing H_2S , it must be done in such a manner so as not to allow air to be introduced into the system. Siphoning is another condition that should not be overlooked in designing the permeate piping for systems without a draw-back tank but with feeds containing H_2S . Once again, the piping arrangement should be designed to keep the RO or NF membrane skid assembly "flooded" and free from air during idle periods.

The precipitation of elemental sulfur on the permeate side does not cause immediate degradation in performance, but over time a gradual increase in feed pressure (net driving force) is observed that can eventually lead to severe loss of efficiency (decrease in specific flux). It is virtually impossible to clean this precipitate from the "backside" of the membrane and permeate channel spacer. Due to the typical aggressive nature of permeate (RO in particular), however, after correcting the situation that caused the problem, just operating the system can restore the loss in specific flux over time, provided there are no other serious fouling problems.

Pretreatment

The best pretreatment for H_2S is keeping the system under anaerobic conditions. The water must not be exposed to air (i.e., oxygen), chlorine or any other oxidizing agents from the well until it exits from the membrane system. H_2S is removed from the permeate (see 'Posttreatment' below). This rule applies to both brackish water and seawater and is of specific importance when iron is present in the ground water. In fact, where it might normally be satisfactory to practice oxidation/media filtration with greensand (glauconite), the presence of H_2S becomes the overriding factor that eliminates this method of iron removal from consideration.

Wells require a check valve to prevent reverse flow back into the well (exception: artesian wells). Back-flow of water into the well will tend to create a vacuum. This can produce voids that will likely cause air containing oxygen to enter the system and oxidize the H₂S. The preferred technique to prevent this is to use submersible pumps with a check valve at the pump discharge in the well. Check valves installed above ground may also work. These check valves must be "bubble tight". If it isn't possible to prevent back-flow into the wells, then a special procedure should be employed upon start up to automatically purge the initial flow from the well to waste. This will help extend the life of the filter cartridges as well as reduce fouling of the membrane.

Treatment of Feedwater Containing Hydrogen Sulfide (cont.)

Post-treatment

Since gasses including H₂S typically pass through RO and NF membranes, it is necessary to remove this objectionable contaminate from permeate as a post-treatment step. The method employed in most membrane systems is air (gas) stripping that employs a forced draft degasifier. This device uses a packed tower with counter current airflow to strip the H₂S out of the water. Note that this process will also remove any CO₂ present (increasing the pH) while saturating the permeate with oxygen, thus exacerbating the inherent aggressive nature of this water. To effectively remove sulfide with this method, it must exist as H₂S. Being pH dependent, this means that either acidification of the feed is done to achieve a permeate pH \leq 6.0 or the permeate is acidified to this point to allow for >90 % removal.

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