

MEMBRANES

TOC REDUCTION USING MEMBRANE TECHNOLOGY

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oneywell's Solid State Electronics Center

(SSEC) in Plymouth, Minn., had been trying to reduce the level of total organic carbon (TOC) in its high-purity deionized water system for many years. They had always experienced periods of relatively low TOC (less than 10 parts-per-billion [ppb]) but always had periods of high TOC (greater than 50 ppb). These high periods had usually been short periods of time and they could not directly correlate the TOC to any contamination on the product. Their water source was from a well via the Plymouth municipal water supply.

In April 1997 everything changed. For the first time, SSEC had a TOC excursion that was long-term. What made the matter more critical is that SSEC could correlate the TOC to contamination of the product. These two things were enough to convince everyone that SSEC had to find a solution that would ensure consistently low TOC levels.

Sequence of Events

The initial response to this problem was to systematically replace all of the consumables that might have been causing the problem. The SSEC brined and burned the two-bed ion-exchange units, regenerated the mixed-bed ion-exchange units, and replaced the activated carbon resin. Ultraviolet (UV) lamps and quartz sheaths in the UV TOC reduction units were also replaced. The

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SSEC then proceeded by sanitizing the reverse osmosis (RO) system and replacing the polisher mixed-bed resin with virgin resin. Unfortunately, none of this had any measurable effect on the TOC levels, as indicated in Figure 1.

The Plymouth municipal water source normally has a TOC level of about 1.5 parts per million (ppm) and the pH level is normally about 7.1. The SSEC did extensive chemical analysis of the city water supply as well as different sampling points in the building and in the supply lines. These initial samples came back inconclusive. The SSEC followed this up by having some samples concentrated and analyzed. These samples came back showing some chloroform and m,p-xylene detected at a concentration below the estimated concentration limit but above the detectable limit. This was the first measurable indication of the source of a problem.

Heat exchangers and other components were isolated in an attempt to find the source of contamination. The SSEC checked the TOC levels in different distribution loops in the building. The DI distribution loops with no use showed lower TOC levels. Once water would start to flow, the TOC level rose from 17 ppb to 52 ppb. It would take several hours of water circulating through the 185-nanometer (nm) UV lights before the TOC level dropped back below 25 ppb. This indicated that the problem was in all the distribution loops and that the problem originated somewhere in the central DI system.

In an attempt to get production going,

SSEC tried trucking in water from another Honeywell division. This tanker system was not able to supply enough water on its own, so plant operators tried a blend of city water and tanker water. By using a blend consisting of 20% tanker water, it was found that they could usually reduce the TOC level to less than 10 ppb as indicated in Figure 2. Analysis of the two water supplies showed the only difference was a higher level of dissolved oxygen in the water that was trucked in. The center also injected oxygen to the raw water supply and achieved the same dissolved oxygen level as the tanker blend, but that did not reduce the TOC level like the tanker blend water did.

As one can imagine, trucking in water was beginning to become a costly enterprise, requiring non-stop labor to keep up. The rental on the three tankers and truck was approximately \$8,000 per week, including the driver. To make matters worse, winter was coming on, and the idea of trying to keep the outside lines from freezing seemed an insurmountable task.

The SSEC then rented an ozone generator system and tried to reduce the TOC by ozonation. This had some effect, but it still could not reduce the TOC to the low levels (less than 10 ppb) that the operations group felt it needed. Low-TOC membranes were purchased for the RO system to attempt to get below the magical 10 ppb level. The new membranes rinsed up quicker than any previous membranes but did not manage to lower the TOC level below 10

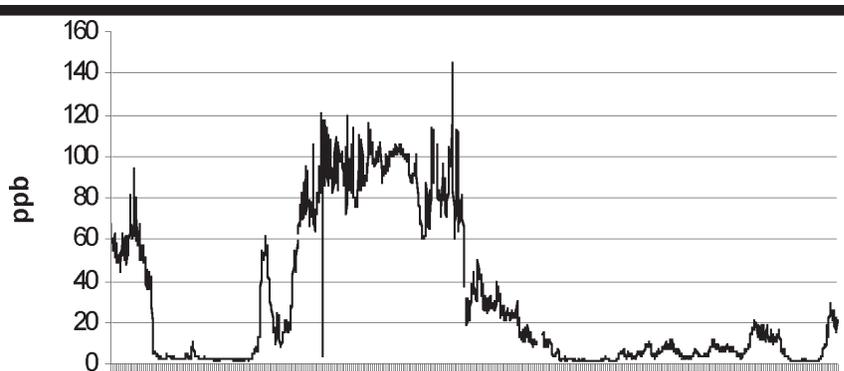


Figure 1. TOC levels in Honeywell SSEC F-loop polisher from 4/30/97 to 5/27/97.

ppb.

The SSEC then chose to drill a well and put it on line for the deionized water system only. The TOC level with the well water was still 80 ppb. The other water parameters were similar to the municipal water supply, which came from wells in the same aquifer.

A vacuum degasifier was considered as an option to try. The two-story height requirement was the main problem with the vacuum degasifier, since SSEC has limited ceiling space in the building. Putting the degasifier outside was not an option since temperatures will go down to -25 °F on occasion during the Minnesota winter. It was decided that the vacuum degasifier was not a viable option for SSEC.

Additional TOC light units were installed in the main DI area. This helped by cutting the TOC level from 80 ppb to about 40 ppb but this action did not allow SSEC to eliminate the expensive blended water process.

The Solution to the TOC Problem

One of the TOC meters being used was equipped with an inorganic carbon removal unit. This unit is designed to remove the inorganic carbon from water with a TOC level of greater than 1 part-per-million (ppm). This particular meter was reading lower TOC levels than any other meter in the plant. This meter should have indicated a higher TOC level because it was hooked up to the RO permeate water, which was upstream of the 185-nm UV TOC reduction lights. At this point, the TOC meter vendor was called in to check out the meter. He brought a manufacturer's rep out with him to look at it. After checking the meter, they determined it to be working correctly. Center personnel asked how the inorganic carbon removal unit worked because they needed to produce it on a large scale. They were told that it was basically a microporous membrane being used with a vacuum pump. Blackford (1), the TOC meter supplier, suggested calling a membrane contactor company for information and to see if they could reproduce the inorganic removal module on a large scale.

Membrane contactors make it possible to transfer gas to or from an aqueous stream without dispersion. The membrane contains thousands of microporous polypropylene hollow fibers knitted into an array that is wound around a distribution tube. The hollow fibers are arranged in a uniform open packing,

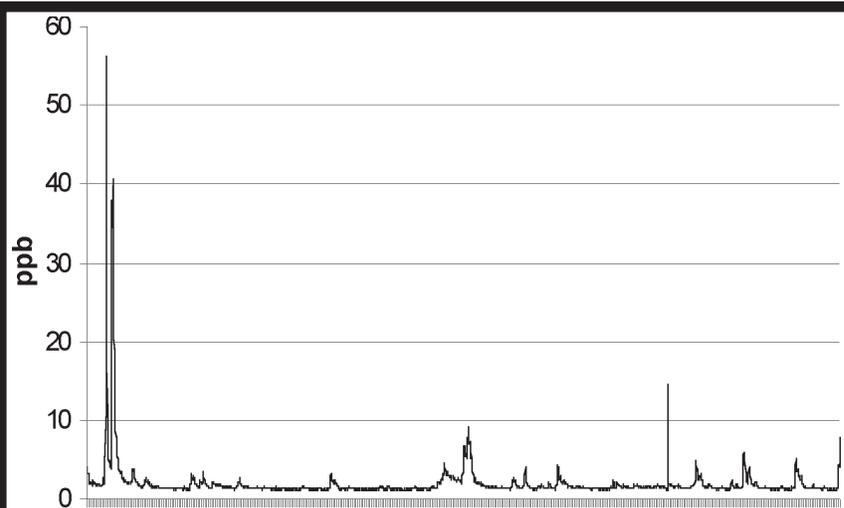


Figure 2. Honeywell, SSEC TOC level in F-loop 10/7/97 to 10/21/97, with tanker water.

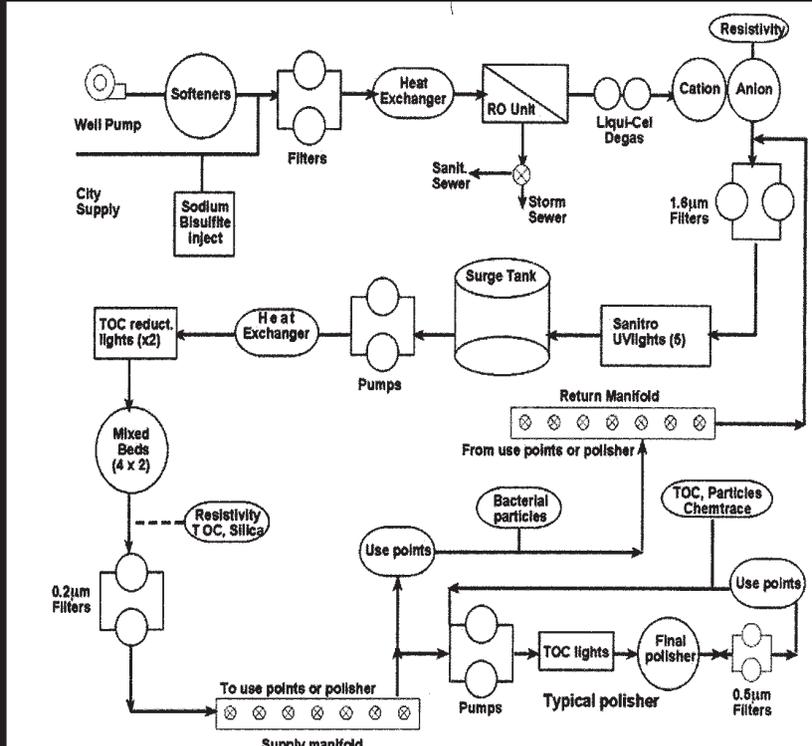


Figure 3. SSEC DI configuration with membrane contactors.

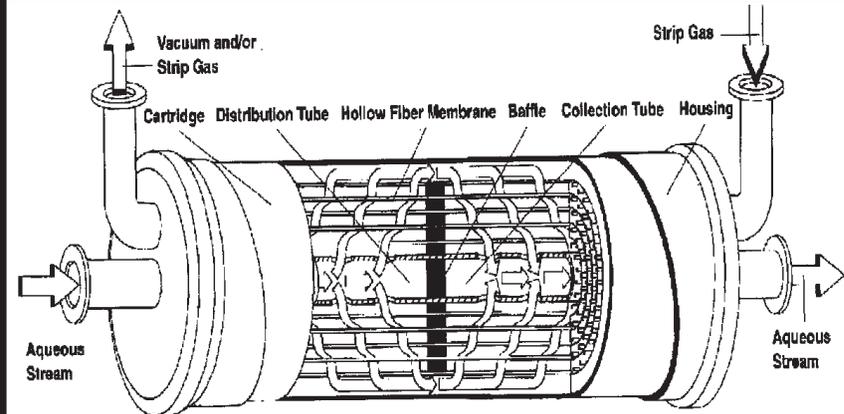


Figure 4. Contactor design.

allowing greater flow capacity and utilization of the total membrane surface area. Because the hollow fiber membrane is hydrophobic, the aqueous stream will not penetrate the pores. The gas/liquid interface is immobilized at the pore by applying a higher pressure to the aqueous stream relative to the gas stream. Unlike dispersed-phase contactors such as packed columns, membrane contactors provide a constant interfacial area for transfer over the entire operating range of flowrates.

Although membrane contactors use a microporous membrane, the separation principle differs substantially from other membrane separations such as filtration and gas separation. With membrane contactors, there is no convective flow through the pores as occurs in other membrane separations. Instead, the membrane acts as an inert support that brings the liquid and gas phases in direct contact without dispersion. The mass transfer between the two phases is governed entirely by the pressure of the gas phase. Because of the hollow fibers and the contactor geometry, the surface area per unit volume is an order

of magnitude higher than traditional contactors. This high level of surface area to volume leads to a dramatic reduction in contactor/system size for a given level of performance.

The membrane manufacturer said that they had never tested and gathered data of this nature and that very little information was known about this. They provided the name and number of someone who might be able to help, Professor E. Cussler at the University of Minnesota. Professor Cussler had done a little research with the removal of trihalomethanes (THM) using membrane technology. Cussler (2) indicated that the microporous membrane contactor worked great on chlorinated organics. A simple pilot study was conducted using a small membrane contactor. This study showed that the TOC levels were significantly reduced. It was estimated that the contactors would be able to reduce the TOC level to below 10 ppb. Honeywell purchased two membrane contactors on May 26, 1998.

The membrane contactors were plumbed in as soon as they arrived at the receiving dock and were on line by

June 1, 1998. As shown in Figure 3, the membrane contactors were piped in a series configuration immediately downstream of the RO system. The membrane contactors are sold as degasifiers. Many people install them for their oxygen removal capabilities. They have a water inlet port, a water outlet port, a nitrogen purge port, and a purge-effluent port (see Figure 4). The membranes were installed based on normal factory recommendations, with minor changes due to space limitations.

The SSEC had a lead-time issue with the correct vacuum pump, so they installed a rotary vane pump to try and get the system running. The rotary vane pump could not handle the high moisture content of the membrane contactor effluent and would overheat within 30 minutes. Because of the problem with the vacuum pumps, SSEC tried the membrane contactors in the nitrogen strip mode, which uses only nitrogen purge gas to strip the gases out of the water and the membrane. The nitrogen strip mode worked well and the TOC level came right down to less than 1 ppb in the final polisher loop, as shown in Figure 5, and has remained there ever since.

The center stopped trucking water as soon as they put the membrane contactors on line. The response was so fast, it was apparent that the problem was solved. As indicated in Figure 6, typical TOC levels in the final polisher loops 6 months after the installation of the membrane contactors were 0.36 ppb. The only time the TOC level has gone above 1 ppb is when piping work is done, and even that is only for a short duration.

An Unexpected Bonus

Before the installation of the membrane contactors, SSEC was getting approximately 100,000 gallons out of the strong acid/strong base two-bed systems before they needed regeneration. This has always been a typical bed life for this system. After flowing 100,000 gallons through the systems, the dissolved silica level in the water coming out of the two-bed systems started to climb and shortly after that the resistivity would start to fall off. After putting the membrane contactors on line, SSEC started getting approximately 600,000 gallons out of each system between regenerations. The reason for the extra capacity in these two-bed systems is that the membrane contactors are removing the carbon dioxide from the water stream. Before the contactors were installed, the

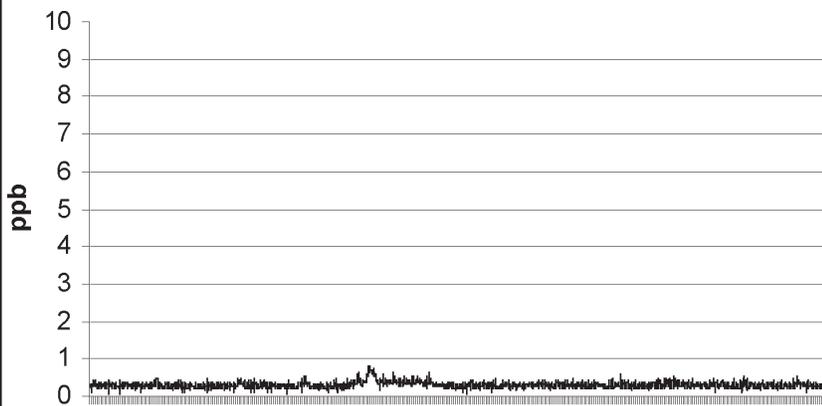


Figure 5. TOC levels in F-loop from 6/6/98 to 6/17/98 after installation of membrane contactors.

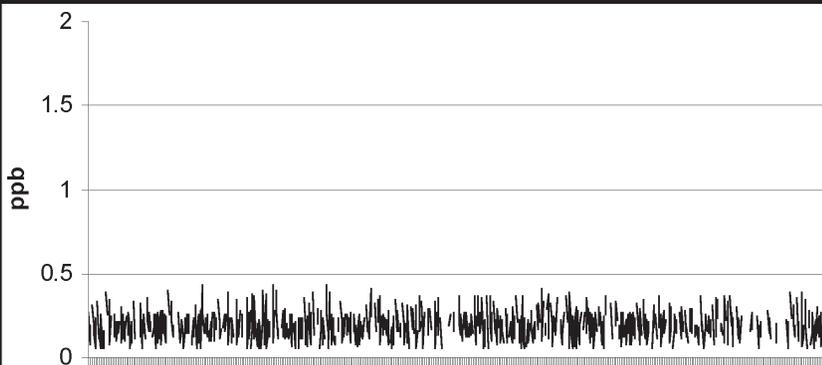


Figure 6. TOC levels in F-loop during January 1999, 6 months after the installation of membrane contactors.

two-bed systems had to remove the carbon dioxide. Now the membrane contactors, which are located just upstream of the IX beds, are taking the carbon dioxide load off. With this major load taken off the two-bed IX systems, they are able to remove more dissolved silica and other contaminants.

The SSEC benefited more from the membrane contactors than was originally anticipated. These benefits include consistently low TOC, reduced dissolved oxygen, and the longer bed life. These benefits have been greatly appreciated by the facilities group and their internal customers.

The SSEC's membrane contactors have been online for more than 1 year. Except for the installation and construction of new equipment, they have not had any instances where they were out of spec for TOC. This is something that was unheard of prior to installing the membrane contactors.

Conclusion

When SSEC decided to go with the membrane contactor solution, they had no concrete evidence it would solve the problem, though all indicators said it would probably help. A major factor in the final decision was the fact that they had systematically eliminated other possible solutions. It was a painstaking and sometimes grueling process, but the end result has been well worth it. The SSEC has found a viable and highly effective solution to the problem of TOC reduction, especially where THM and chlorinated organics are a concern.■

References

1. Blackford, D., Fluid Measurement Systems, Vadnais Heights, Minn., personal communication (May 12, 1998).
2. Cussler, E., University of Minnesota, Minneapolis, Minn., personal communication (May 22, 1998).

Endnotes

The membrane devices used in this system are Liqui-Cel Membrane Contactors manufactured by Celgard Inc. in Charlotte, N.C.

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Key words: DEGASIFICATION, DI WATER, ION EXCHANGE, REVERSE OSMOSIS, SEMICONDUCTORS, TOC