CLEANING COMPOUNDS

CASE STUDY FOR UHP PIPING SYSTEM SANITIZATION: A SEARCH FOR AN EFFECTIVE SANITIZING AGENT TO REDUCE SYSTEM DOWNTIME

Ultra-high-purity (UHP) water piping-loop distribution systems require periodic sanitization when bacteria, total organic carbon (TOC), and particle levels reach a predetermined unacceptably high limit. This case study presents our experience with three sanitizing agents — hydrogen peroxide, peracetic acid/hydrogen peroxide, and quaternary ammonium compound — that were used at our facility.

Based on our results, when the overall utility of these sanitizers was compared, we found that the quaternary ammonium compound was the most cost-effective sanitizer used. This conclusion was based on the overall effectiveness of the sanitization, the rinsability characteristics of the compound, and the saving of hundreds of hours of production downtime.

In the fall of 1988, our semiconductor manufacturing facility in Durham, N.C., began installing a two-phase high purity water system. Phase I as planned was to be a 120-gallon-per-minute (gpm) point-of-use system. Phase II was to enlarge the system to a capacity of 300 gpm.

Major Components

The major system components were reverse osmosis (RO); primary, secondary, and mixed-bed polishing deionization; submicron filtration; ultraviolet bacteria and TOC reduction; and ultrafiltration. On-line monitoring was done for the following critical parameters: silica, sodium, particles, TOC, resistivity and conductivity, pH, and temperature. Off-line data collected consisted of bacteria and particle counts (at 0.2 µm), and fluorescent microscopy.

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The Phase II enlargement program was conducted during four shutdowns in 1989 and 1990. During this program, I was asked to shorten the time needed for a complete piping-loop sanitization during shutdown. I decided to test two new system sanitization products: a prepackaged compound of peracetic acid and hydrogen peroxide, and a speciality quaternary ammonium compound specifically formulated for high-purity piping system sanitizations.

Successful sanitization of a high-purity system is not simple. Both the effectiveness and the system component compatibilities of the chemical agent selected must be considered. My experience has shown me that any sanitizing agent can potentially cause problems. In order to avoid obvious problems, it is necessary to bypass or isolate equipment components that could be damaged by the sanitizing agent selected. System components to be avoided include: RO, ion-exchange, and production equipment; monitors; and ultrafilters. Neglecting to bypass the RO system could shorten the life of the membranes. An oxidizer will shorten the throughput capacity and reduce the moisture-holding capacity of the ion-exchange resins. If oxidation of the resin occurs, regeneration costs will increase and regeneration quality will decrease. In addition, TOC values coming from the DI units will become unstable and will fluctuate with variations of TOC in the incoming water.

Three Sanitizations

At our facility there were three system sanitizations during the start-up and completion of Phase I, the 120-gpm system. All of these cleanings utilized 5% hydrogen peroxide as the chemical agent. Setup for a typical high-purity-water system sanitization requires at least six to eight weeks of detailed advanced planning and preparation. One must consider what effect hydrogen peroxide may have on the process equipment. To ensure that no damage will occur, isolation valves must be double- and triple-checked.

As a minimum, the following checklist should be considered:

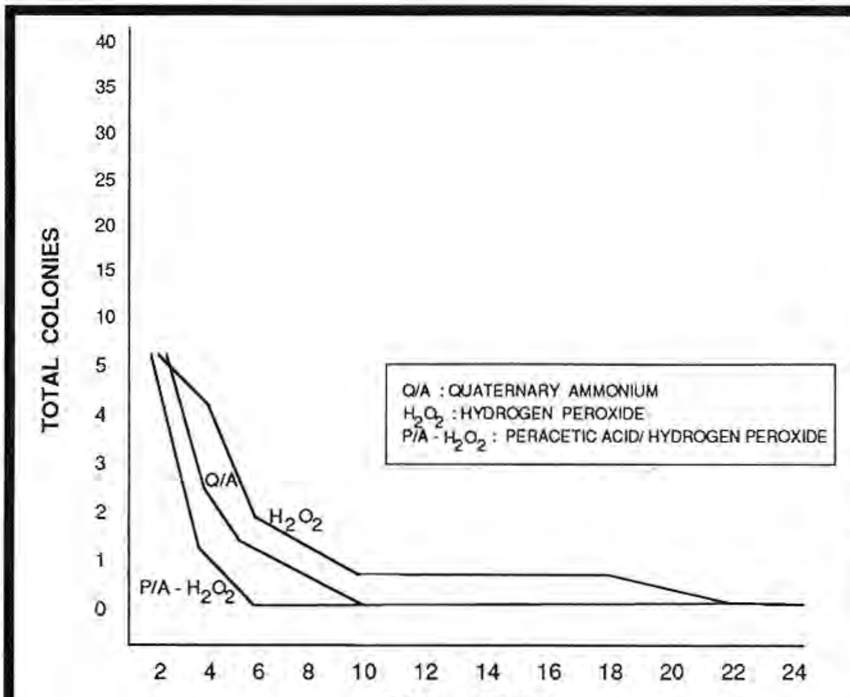

Figure 1. Recirculation time versus bacteria colonies.

- Safety of personnel and equipment
- Detailed sanitization procedure planning
- Sanitizing agent's chemical compatibility with all system components
- Sanitizing agent's recirculation time
- Bypass procedures for production equipment, RO, ion-exchange resins, and ultrafilters
- Changing of UV lamps while cleaning agent is recirculating
- Cleaning or changing of quartz sleeves
- Change of filters after thoroughly rinsing sanitizing agent level down to 1 to 2 parts per million (ppm)
- Confirmation with local city officials before sending any chemical into the sewer system
- Rinse-up time projections
- Required on-line specifications for the RO and ion-exchange equipment
- Time required to clean ultrafiltration modules
- Specifications for production equipment to go back on-line

Rinsing the system begins following recirculation of the sanitizing agent for the prescribed time. When using hydrogen peroxide this step may take from 12 to 24 hours, and requires careful monitoring of the sanitizing agent left in the piping loop. Potassium permanganate is commonly used to determine the low-level presence of hydrogen peroxide in the piping loop, but the sensitivity of potassium permanganate is questionable. At Mitsubishi, we use hydrogen peroxide test strips. In our experience, when potassium permanganate shows that the rinse-up is complete, the hydrogen peroxide test strips will show a 2- to 3-ppm level.

I believe it is at this time that damage to the DI resin and process equipment occurs. It is my experience that all ion-exchange units have small dead legs at the inlet and outlets. These dead legs hold low levels of hydrogen peroxide for extended periods of time, depending on the pipe size. It has been found that dead legs are located not only where piping runs stop, but also where valves, sample ports, gauges, and low flow areas exist. The next time you sanitize your system, check a rinsed-out dead leg an hour later. You may find hydrogen peroxide present again.

We monitored our system at rinse-up for resistivity, TOC, and particles. After using hydrogen peroxide, resistivity and particles were never a problem. TOC, however, stayed high for a couple of days; and it took from 1 to 3 weeks to come down to our required specifications. To shorten the time required for hydrogen peroxide system sanitizations in the past, we reduced the chemical recirculation time and increased system flowrates and pressure. Faster rinse-up times were achieved when we opened the return bypass, which allowed return flows to go to our waste treatment holding tank. This allowed only fresh water to go into the system.

These procedural changes all shortened the time required to complete a hydrogen peroxide sanitization, but they did nothing to shorten the time required to achieve required TOC levels.

Alternate Sanitizing Agents

Because of the drawbacks associated with the use of hydrogen peroxide for piping-loop sanitizations, we decided to look at alternative sanitizing agents. In July 1989, we tried a new sanitizing solution that contained peracetic acid and hydrogen peroxide. The chemical recirculation time was 12 hours. Rinsing up the system took approximately 14 hours. Resistivity and particle levels after rinsing were well within specifications. The TOC levels were 200 parts per billion (ppb) after rinse-up, and took eight days to decrease to a level below 50 ppb. Even though this was an improvement over using hydrogen peroxide, we still found a hydrogen peroxide residual in the system's dead legs. Bacteria counts over the next six months stayed within specifications. This sanitizing compound came with a working-level and rinse-level test kit, and was reported by the manufacturer to be filtered.

Still in our quest for a better system sanitizer, at the December 1989 shutdown we tried a high quality quaternary ammonium (Q/A) sanitizing compound, specifically formulated for high purity water system requirements. This cleaner was of extreme interest because it does not contain any oxidizing agents. We think this is important because the Q/A compound will not destroy ion-exchange resins as do compounds containing hydrogen peroxide. In fact, should low levels of the Q/A compound contact the resin, it will not have any permanent detrimental effect on capacity.

A normal resin regeneration will bring the resin back into specifications. The cost of regeneration is less than the cost of replacing resin. We recirculated the Q/A solution for 12 hours. This rinse-up time was 12 hours. During the rinse-up,

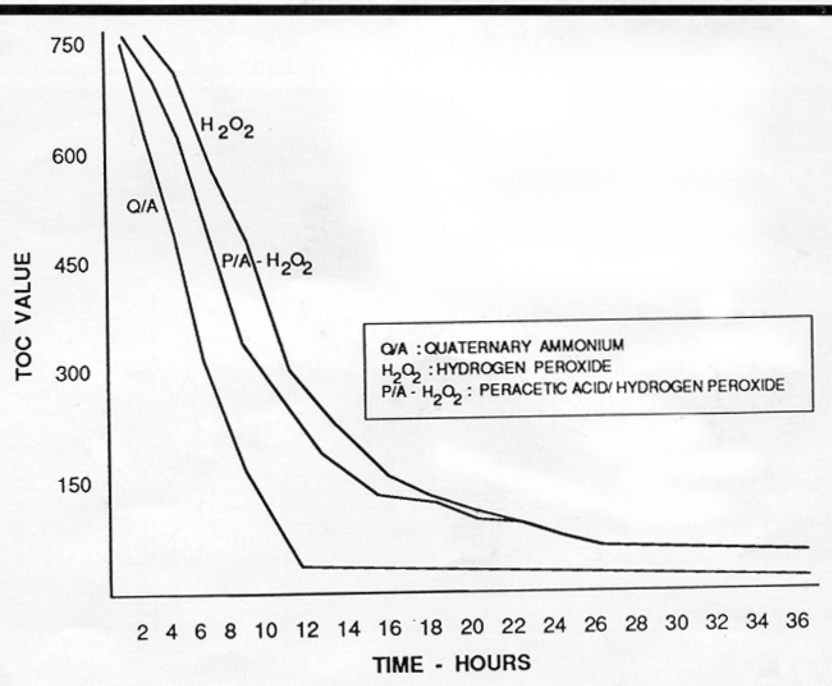

Figure 2. Total organic carbon reduction.

TOC started at 650 ppb, and within 30 hours the value dropped to below 50 ppb. One week later bacteria samples were taken. All samples were within specifications during the first 36 hours after rinse-up. Over the next six months we monitored bacteria (48 samples taken weekly) and particles. Bacteria colonies were less than 5 colony forming unit per milliliter and particles were less than 5 at 0.2µm.

Since we were pleased with the results from December 1989, in July 1990 we again used the high quality Q/A compound for system sanitization. Recirculation time was again 12 hours and the rinse-up time was reduced by 4 hours. We achieved this by sending all return flows to drain. When the Q/A solution in the rinse water had a value of 2 to 3 ppm, we put one primary and one secondary mixed bed on-line. Resistivity rinse-up times were cut by four hours, and particle rinse-up times were cut by two hours. TOC was less than 50 ppb within 24 hours of the start of rinsing. Bacteria colonies were checked one week later and again were well within specifications.

Continuing to get excellent results, we again used the Q/A solution for our December shutdown of 1990. Trying to fine tune the procedure, we decided to cut the recirculation time by 6 hours. As a result, we found that the resistivity, TOC, and particle numbers were excellent. We did notice that the bacteria numbers were 20% to 25% higher than after the two previous Q/A sanitizations.

* The high quality ammonium (Q/A) compound referred to throughout this paper is Microclean UHP from King Lee Technologies.

New Study

We are presently doing a study on bacteria and TOC. Our test data shows bacteria to be within specifications if the recirculation for the Q/A sanitization is 10 hours or more. On our next sanitization with this Q/A compound, recirculation time was 12 hours. Test data is too new to be concrete at this time, but bacteria colonies and Q/A recirculation times are strongly related. The high quality quaternary ammonium compound we use has been specifically formulated for high purity pipe applications, and comes with working- and rinse-level test kits.

The rinse-level test kit is difficult to read when the Q/A in the rinse water drops below 2 ppm. The Q/A compound we use is compatible with all plastics and stainless steel system components. It is not recommended to run this agent through the RO unit, however, as some interaction with the membrane may occur. When using this product, it is advisable to replace the final filters after rinsing the system down to a Q/A residual of 2 to 3 ppm. The Q/A does not harm the filter material, but it can lead to long rinse time because of its excellent surface activity.

Figures 1 and 2 summarize the data presented for the three sanitizers used. Figure 1 shows the reduction in bacteria colonies versus sanitizer recirculation time; Figure 2 shows TOC reduction versus on-line time after sanitization.■

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