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Surface Preparation: Pure & Ultra-Pure Water

A material common to nearly all cleaning processes is water (H_2O). It is used to prepare cleaning and etching solutions and to perform a final rinse to remove materials that might leave a residue on the cleaned surface after drying. Contaminants that may be present in water are: ions of atoms and molecules, dissolved organic materials, biological agents, and particulates. The type and amount of contaminants in the water depends on the source of the water and can vary with time. Natural "hard water" contains metal ions, such as iron, calcium, manganese, and magnesium, which can form water-insoluble salts by reacting with cleaning agents such as soaps. Natural "soft water" is water that is relatively free of metal ions but may contain dissolved organic materials and biological agents. A type of soft water is produced in a "water softener" by exchanging the metal ions that can form insoluble salts with sodium ions from sodium chloride (NaCl). The NaCl is water soluble; however, it will leave a residue when the water is evaporated.

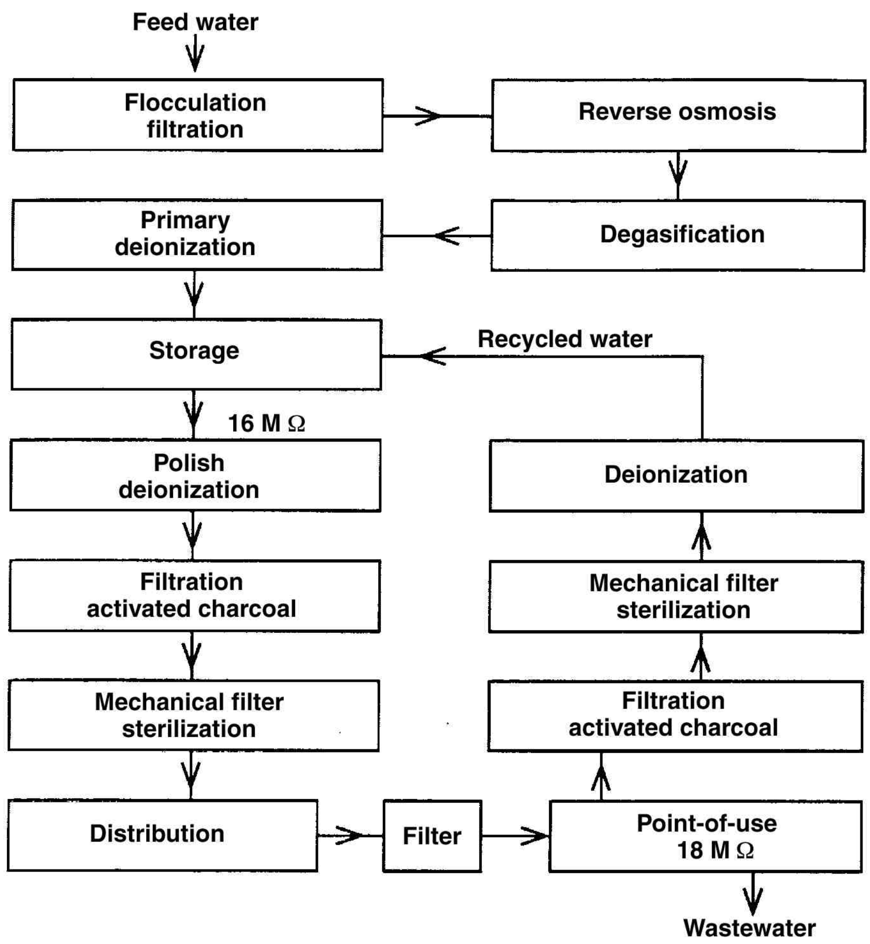

Fig. 1—High-volume ultra-pure water production facility.

"Pure" Water

One solution to purify water is to distill (or "doubly distill" or "triply distill") the water. Such water is relatively expensive but is commercially available and used for sanitary applications, such as rinsing contact lenses. This source may be useful if only small amounts of purified water are needed. Unfortunately, commercially produced distilled water is often stored in plastic containers from which the water can leach organic materials that will leave residues when evaporated.

Commercial "pure water," such as "spring water" or "RO water," is prepared by reverse osmosis (RO) through a semipermeable membrane. RO purification had its beginnings in the early 1970s using hollow-fiber (cellulose acetate or polyamide) reverse-osmosis technology. The hollow-fiber membranes required a pressure differential of 350–450 psi to give a reasonable output of purified water.

In the early 1980s, a thin-film composite membrane was developed that revolutionized water purification.

For the first time, reverse osmosis could operate at a pressure differential as low as 250 psi and still produce reasonable output. These membranes were formed by casting an ultra-thin active layer of polyamide material on a highly porous polysulfone substrate. This membrane structure replaced the hollow-fiber reverse-osmosis technology because the lower operating pressure saved energy, which had been the biggest cost factor in reverse-osmosis purification.

In the latter part of the 1990s, new “low-pressure” varieties of RO membranes appeared on the market. The current state-of-the-art membranes operate at 130–150 psi on most municipal water supplies. The semipermeable membrane (pore size of 10^{-3}–10^{-4} microns) rejects dissolved solids (90–98%), dissolved organic materials (99%), particulates, and most biological agents; though some biological agents can grow through the membrane if it is not maintained properly. Chlorine ions in the water can degrade the membranes.

The industry standard for measuring the performance of reverse-osmosis membranes is 1500 ppm sodium chloride solution that has an osmotic pressure of 15.5 psi. With more dissolved impurities, the operating pressure will be higher because the pure water must overcome the osmotic pressure in addition to the flow-resistance of the membrane material. For example, in seawater desalination applications, the osmotic pressure of the seawater is 410 psi, and the water pressures needed are 850–950 psi.

Unfortunately, commercially produced RO water is often stored in plastic containers from which the water can leach organic materials. Small RO purification units cost only a few hundred dollars and are a good source of pure water for many applications.

Ultra-pure (DI) Water

Ultra-pure (or “semiconductor grade”) water (UPW) has all types of contaminants reduced to a very low level. ultra-pure water is often called deionized water (DI water) because the most commonly measured contaminant is the ionic content of the water. DI water, however, may contain significant amounts of non-ionic contaminants. To prepare ultra-pure water, ion exchange resins are used to remove ions. These resins remove ions by exchanging H^+ for cations and OH^- for anions. In some cases, particularly when high volumes of water are required, the ion-exchange resin columns are preceded by a reverse-osmosis system that increases the life of the exchange resins. These resins must be replaced periodically. The end-of-life of the resins is indicated by silica or borate “breakthrough.”

To remove organic materials, the water is filtered through activated charcoal filters. Inert mechanical filters remove particulates and biological agents. Mechanical filters should be made of a fluoropolymer such as Teflon™. Filters may be staged from larger to smaller pore size and should have a final pore size of 0.2 microns. The filters collect biological agents that can grow on the filters and plug the pores. These biological agents should be killed using ultraviolet light from a mercury lamp (254 nanometer wavelength) or ozone dissolved in the water. The shorter wavelength UV from a mercury vapor lamp (185 nanometer wavelength) destroys ozone by converting it to diatomic oxygen and ionizes organic materials, making them easier to remove by the ion exchange resins. A disadvantage of UV, however, is that it degrades fluoropolymers.

Spontaneous dissociation of the water molecule to OH^- and H^+ limits the resistivity of ultra-pure water to about 18.2 megohms between electrodes spaced one centimeter apart (18.2 megohm-cm) at room temperature. This is equivalent to about five parts per billion (ppb) of NaCl. Electrical conductivity measurements do not measure the organic, particulate, or biological contamination, and other analysis techniques must be used to measure these impurities. Particle content can be measured by light scattering. Organic material can be determined by evaporation and residue analysis. Biological agents can be detected by culturing the agents, but this takes time. If ultra-pure water is exposed to the atmosphere, it will absorb CO_2, forming carbonic acid (H_2CO_3), which will disassociate and decrease the electrical resistivity. Care must be taken that the ultra-pure water is not contaminated by storage and distribution systems.

Specifications for ultra-pure water can be as stringent as:

- Resistivity—18 megohm-cm continuous at 25°C
- Particle count—less than 500 particles (0.5 microns or larger) per liter
- Bacteria count—less than one colony (cultured 48 hours) per cc
- Organic material—less than one part per million by weight (ppmwt)

Ultra-pure water must be produced in quantities that satisfy both the continuous and the peak-level use requirements. High volumes of ultra-pure water are made by:

- Pretreatment—pH adjustment, flocculation, filtration
- Reverse osmosis—removes most contaminants
- Degasification—removes dissolved CO_2
- Ion exchange (anion & cation)—removes ionic contaminants
- Adsorption materials (activated carbon)—remove organic materials
- Mechanical filtration—removes particulates and biological matter
- Ultraviolet radiation or ozone bubbling—kills biological agents on the filters
- Point-of-use filtration—0.2-micron filter pore size

Figure 1 shows one arrangement for producing high volumes of ultra-pure water. Slightly contaminated water can be recycled by “polishing” the water. Smaller amounts of ultra-pure water can be prepared by the same processing steps, beginning with the ion-exchange process.

Ultra-pure water should be stored and distributed in materials that contain no extractable materials and do not support the growth of biological agents. The best container materials are fluoropolymer materials, such as PETFE (Teflon™) or ECTFE (Halar™). High-density polyethylene and polyethylene terephtalate (PET) can be used for storing ultra-pure water, but low-density polyethylene is porous and should not be used. Unplasticized polyvinyl chloride (uPVC) piping, or equivalent, should be used to distribute ultra-pure water. The uPVC should be heat-bonded or thermal-welded instead of glue-bonded. Metal should be avoided since the ultra-pure water will take metal ions into solution. Common chemical laboratory tubing such as Tygon™ should not be used since it has a high content of leachable organic materials.

In distribution systems, the water should be continuously flowing or be allowed to flow before use, and the electrical conductivity measured at the point of use. It is not uncommon for the distribution system to become contaminated with biological agents that are difficult to remove. Ultra-pure water should be heated by Teflon™-coated heaters. It should never come into contact with metal surfaces for any length of time.

In some cases, RO water can be used for most applications, then ultra-pure water used for the final rinse. In a cleaning operation, surfaces should never be allowed to dry before a final rinse in ultra-pure water. The surface should be rinsed until the rinsewater attains a specified resistivity (*e.g.*, 5 megohm-cm, 10 megohm-cm, 15 megohm-cm, etc.). This procedure is called “rinse-to-resistivity.” In many rinsing operations the surface is rinsed in successively more pure water (“cascade rinse”). This can be done using spraying or rinsing in a tank.

Rinse tanks are often agitated ultrasonically or with fluid jets. At each stage, the water should be continuously filtered, and when rinse tanks are used, the water should flow over the lip of the tank to carry away particulates and low-density contaminants, such as oils, which can accumulate on the surface. This prevents the contaminants from being “painted-on” the clean surface as it is withdrawn from the rinse tank.

Water is often used in conjunction with a wetting agent, such as alcohol, to lower the surface tension of the water. For example, water has a surface energy of 73.05 dyne/cm, while a mixture of water plus 50-percent isopropyl alcohol has a surface energy of about 27 dyne/cm. The lower surface energy allows the water to penetrate easily into small pores and cracks, and decreases the size of stable water droplets. Small droplet size makes for more efficient “blow-drying.” P&SF

Reference

M.K. Balazs, “A summary of new methods for measuring contaminants in ultra-pure water,” *Microcontamination* **5**(1) 35, 1987.