Measuring and removing dissolved and colloidal silica in ultrapure water

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Most semiconductors are made by chemically processing the surface of a single crystal of silicon. Between each manufacturing stage, chemicals used in the previous stage must be rinsed from the wafer surface with ultrapure (UP) water. As a silicon wafer is processed, as much as 5000 L of UP water may be used to wash the wafer's surface. Any impuri-

A promising new technique for ultrapure water systems combines ultraviolet radiation and ozone to remove colloidal silica by converting it into dissolved silica.

ties present in the wash water may remain on that surface after the UP water has evaporated. Even minute traces of contamination on the wafer's surface can cause defects in the resulting semiconductor device. It is therefore imperative to use water of the highest purity.

Perhaps the single most difficult contaminant to remove from UP water is silica. Silica can exist in three physical/chemical forms: monomeric (dissolved/soluble/reactive), polymeric (colloidal/unreactive), and granular (particulate). UP water may contain silica in any of these three forms, and the forms may

change from one to another, depending on the water's acidity/alkalinity.

Dissolved silica affects the thermal oxidation process on the wafer surface. Colloidal silica, which is defined as having a particle size of <100 nm, can act as an unwanted bridge between conducting surfaces. Dissolved silica may also interfere with gate composition and change the electrical characteristics of a device, rendering it useless. Deposited colloidal silica can also act as nucleation sites for other particles. To illustrate the contamination potential of colloidal silica, one study reports that 1 ppb by weight of colloidal silica equals 100 million 20-nm-diam particles per milliliter.[1]

Measuring Silica in Ultrapure Water

The amount of reactive and unreactive silica in UP water can be determined by various analytical methods, including gravimetry, colorimetry, graphite furnace atomic absorption spectroscopy (GFAAS), scanning electron microscopy (SEM), ion chromatography (IC), inductively coupled plasma–mass spec-

troscopy (ICP-MS), and inductively coupled plasma–atomic emission spectroscopy (ICP-AES).

Measuring Dissolved Silica. The most common method for measuring low levels of dissolved silica (<2 mg/L) is colorimetry. A sample of water is mixed with ammonium molybdate in an acid medium. Any reactive or dissolved silica reacts with the ammonium molybdate to form a yellow silicomolybdate complex. Amino or ascorbic acid is then added to create an intense heteropoly blue color. The degree of blueness is directly proportional to the amount of silica in the sample. This sequential batch sampling method can report up to six measurements per hour and is available from several suppliers as an automated instrument.

Measuring Total Silica. Total silica is measured by either GFAAS or ICP-MS. In GFAAS, a water sample is vaporized and reduced to individual atoms by thermal decomposition in a graphite tube furnace. The majority of atoms are in the ground state and readily absorb characteristic wavelengths of light. The amount of light absorbed by the silicon atoms indicates the total silica content in the water sample. In ICP-MS, a high-frequency inductive coupling plasma is used to ionize the sample. A nebulizer sprays the water sample into an argon plasma at 6000 K. In the argon plasma, the nebulizer droplets are vaporized, atomized, and ionized. The ions generated are then passed into a mass spectrometer where they are identified and measured, based on their mass-to-charge ratios. Because of the high cost of GFAAS and ICP-MS tools, the measurement of total silica by either of these methods is generally considered an off-line procedure; in most cases, a water sample is transported to a lab for analysis.

Measuring Colloidal Silica. The amount of nonreactive or colloidal silica can be estimated by subtracting the value of the dissolved silica from that of the total silica. There is no direct method of measuring colloidal silica since the size of most colloidal silica particles is smaller than even the 50-nm detection limit of the most sensitive liquidborne particle counters. However, the nonvolatile residue monitor (NRM),

a recently introduced instrument designed to continuously measure nonvolatile residue, has demonstrated the ability to measure colloidal silica down to <20 nm.[2] The colloidal silica is detected as a component of the overall residue obtained from UP water by a spray/evaporation and residue agglomerate recovery technique. This technique cannot distinguish between the various sources of residue — including colloidal and dissolved silica — but it can detect overall residue contamination as low as 10 ppt.

Combined Use of a Colorimetric Analyzer and NRM

An on-line Model 651C dissolved silica analyzer using the molybdate colorimetry technique (Hach, Loveland, CO) and a Model 7761 NRM (Particle Measuring Systems, Boulder, CO) were employed to obtain as complete a measurement of silica as possible. To demonstrate the instruments' response,

While not perfect, the combined use of an on-line silica analyzer and NRM can provide nearly real-time, detailed information of dissolved, colloidal, and total silica.

an experiment was performed with both dissolved and colloidal silica challenges. (Nissan Chemical and DuPont colloidal silica with sizes of 5, 11, 22, 65, and 85 nm were used in the experiment.) The results are shown in Figure 1. As expected, both instruments detected nearly 100% of the dissolved silica. Also as expected, the silica analyzer did not detect any colloidal silica. The NRM detected colloidal silica with decreasing efficiency as the particle size increased. This performance characteristic is contrary to that of conventional particle counters, which show greater detection efficiency as the particles get larger. The NRM's somewhat anomalous behavior is explained by the fact that at smaller sizes (<20 nm), the colloidal silica starts to behave more like residue and less like discrete particles. Figure 2 illustrates the excellent linearity of the NRM's response to increasing concentrations of various sizes of colloidal and dissolved silica.

Figure 3 shows the response time of the silica analyzer and NRM to a 10-minute pulse of dissolved silica. Both instruments detect the silica in approximately 7 minutes, with detection levels rising to more than 90% after approximately 15 minutes. Both instruments show almost ideal response to a pulse change in dissolved silica. While not perfect, the combined use of these two on-line detectors can provide nearly real-time, detailed information of dissolved, colloidal, and total silica.
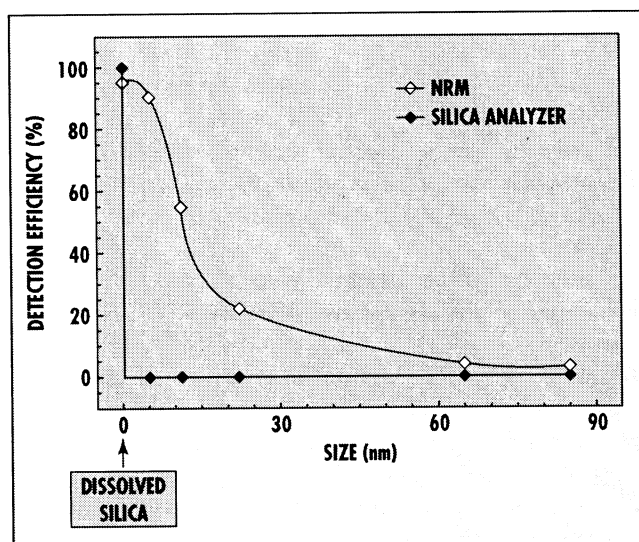

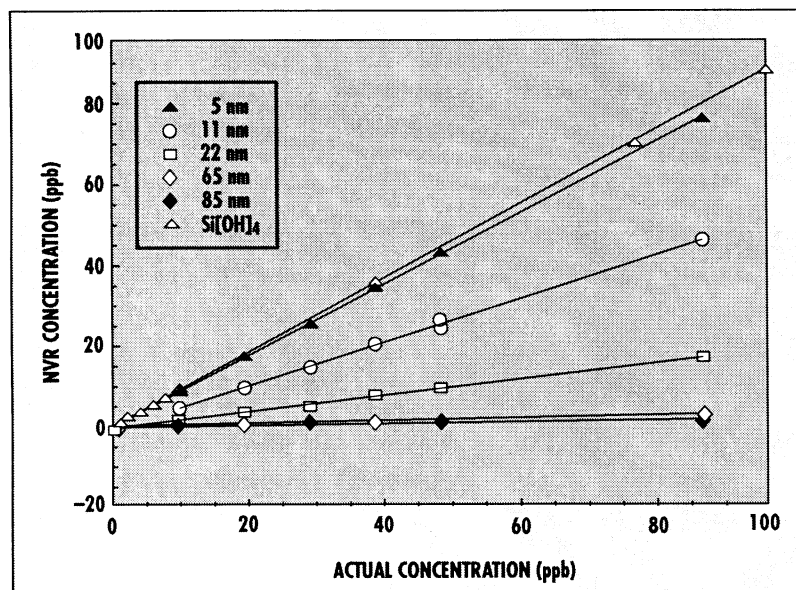**Figure 1: Detection efficiencies of NRM and silica analyzer for dissolved and colloidal silica.**

Figure 2: Linear response of NRM to increasing amounts of colloidal and dissolved silica.
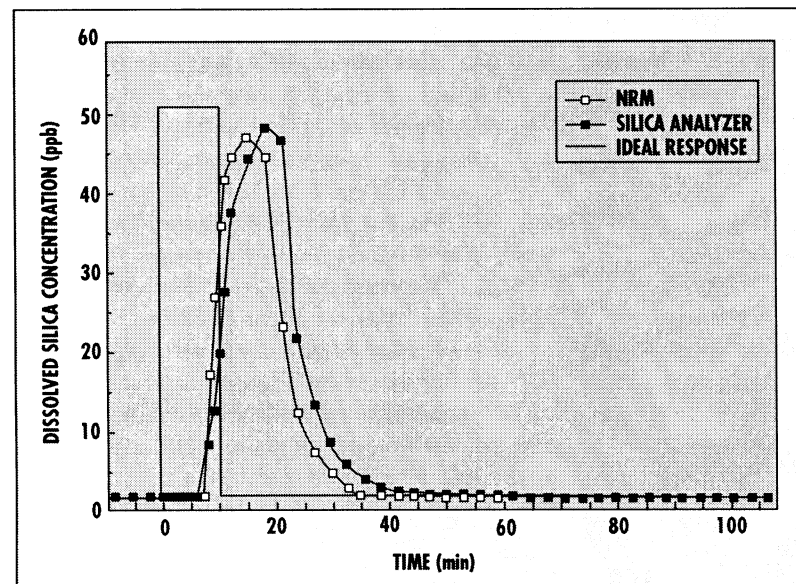

Figure 3: Response of NRM and silica analyzer to 50-ppb pulse of dissolved silica.

Silica Removal Methods

There are three methods for removing silica from water: reverse osmosis, ion exchange, and filtration.

Reverse Osmosis. Reverse osmosis (RO) is a physical process in which a semipermeable membrane removes primarily dissolved materials from water. By applying to the feedwater a pressure greater than the natural osmotic pressure, the membrane preferentially allows water molecules to pass through and rejects a high percentage of dissolved silica and similar materials. If the membrane's pore size is small enough, RO membranes can also remove colloidal silica. However, even a membrane with a 200-molecular-weight cutoff can allow significant amounts of colloidal silica to pass through.

Ion Exchange. Ion exchange is the interchange of ions between a solid resin bead and water passing through a bed made of resin beads. Ion-exchange resins can either be prepared from synthetic polymers to form either acidic cation exchange sites or strong basic anion-exchange sites. Ionic contamination in the water—such as dissolved silica—is preferentially exchanged for hydroxyl ions on the resin and thereby effectively removed from the water supply.

In certain applications, strong base macroporous resins with a honeycomb structure can also remove colloidal silica. The removal mechanisms are unclear, but it is thought that the large pores of the resin physically capture and entrap the unwanted colloidal silica by electrostatic attraction.[3] However, others believe that the removal mechanism is both physical and chemical.[4] As the colloid enters the porous structure of the resin, it begins to dissolve because of the basicity of the hydroxyl radical. The dissolving colloidal silica penetrates the pores of the resin, leaving additional space for more colloidal silica to enter. However, even a porous resin has a limited capacity for colloidal silica removal. As the resin sites become full—that is, the resin becomes exhausted—silica leakage occurs because the resin starts to release previously captured material. Colloidal silica is one of the first materials to be discharged because it is only loosely held; it is closely followed by dissolved silica.

To observe how effectively ion-exchange resins can remove dissolved and colloidal silica, an experiment was performed using a highly regenerated Ionac NM-60 mixed-bed resin (Purolite, Bala Cynwyd, PA). Dissolved silica was injected at sequential levels of 15, 30, and 50 ppb into a polishing loop where the ion-exchange bed was bypassed. Silica levels were measured by the NRM and allowed to stabilize. The ion-exchange bed was then reinstalled while dissolved silica continued to be injected at the

As the resin sites become full, silica leakage occurs because the resin starts to release previously captured material.

previously mentioned levels. The results of this experiment are depicted in Figure 4. Within 25 minutes, the ion-exchange bed effectively expunged all traces of dissolved silica and the NRM returned to background water levels. This experiment
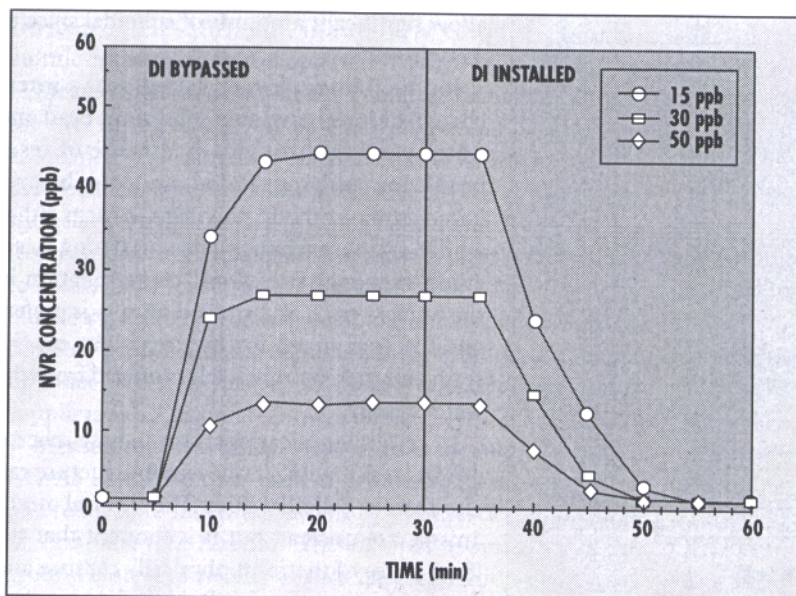
Figure 4: Removal of dissolved silica by mixed-bed deionizer (DI).
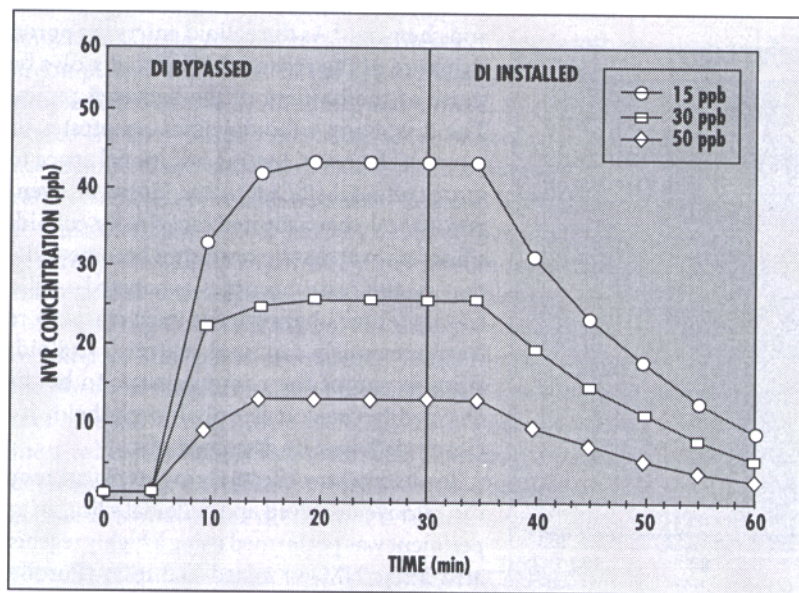

Figure 5: Removal of colloidal silica by mixed-bed deionizer.

dramatically illustrates how effective ion-exchange resins can be at removing dissolved silica from water.

The experiment was repeated with 5-nm colloidal silica, which was sequentially injected at 15, 30, and 50 ppb and allowed to stabilize. Once again the ion-exchange bed was reinstalled while colloidal silica continued to be injected. As the results in Figure 5 show, the ion-exchange bed removed most of the colloidal silica, but a significant fraction (approximately 20%) remained after 30 minutes. These results illustrate that while newly regenerated ion-exchange resins can remove most colloidal silica, the removal efficiency is much lower than that of dissolved silica removal.

The performance of the ion-exchange resin for colloidal silica removal degrades rapidly, resulting in colloidal silica leaching. To illustrate this point, 11-nm colloidal silica was in-

jected into a partially exhausted ion-exchange bed at 50 ppb as a step function on three consecutive days and the output of the ion-exchange resin was monitored by the NRM. The results, shown in Figure 6, confirm that on each successive day the ion-exchange resin allowed an increasing amount of colloidal silica to penetrate the bed. When this same experiment was repeated for dissolved silica, no breakthrough was observed. This further confirms that ion-exchange resins both remove and retain dissolved silica much more efficiently than colloidal silica.

Filtration. Two filters have shown potential for removing colloidal silica: charged modified filters and ultrafiltration membranes. A charged modified filter uses the forces of electrical attraction in addition to the conventional filtration mechanisms of interception, impaction, and diffusion to capture submicron-sized colloid particles. Colloidal silica is negatively charged in water. Positively charged modified filters have removed colloidal silica while maintaining a low pressure differential.[5] In another study, the NRM and colloidal silica challenges were used to evaluate filter performance for commercially available filters with pore sizes from 0.1 to 0.004 μm.[1]

Ultrafilters are cross-flow membranes similar to RO membranes. Ultrafilters operate at much lower pressures (2–6 bar) than RO membranes (10–30 bar) and tend to have larger molecular-weight cutoff. Ultrafilters are intended for final polishing and pyrogen removal but can also remove colloidal silica. A double-skinned, hollow-fiber polysulfone membrane with a 10,000-molecular-weight cutoff successfully removed colloidal silica >7 nm.[6]

Using the above-mentioned removal techniques, UP-water systems can deliver water with very low levels of dissolved silica. However, the effectiveness of these techniques for removing colloidal silica is at best marginal. New, more potent methods for such removal need to be developed.

Generation of Dissolved Silica within UP-Water Systems

Most UP-water systems contain a component that can add dissolved silica to the water. Ultraviolet radiation is commonly used to control bacteria (254-nm wavelength) and destroy total organic carbon (185-nm wavelength). The UV bulbs are housed within quartz sleeves. Figure 7 shows the effect of 185- and 254-nm UV wavelengths on downstream levels of dissolved silica over 3 hours. Dissolved silica levels were allowed to accumulate within a recirculating loop. Significant levels of dissolved silica were generated with 185-nm
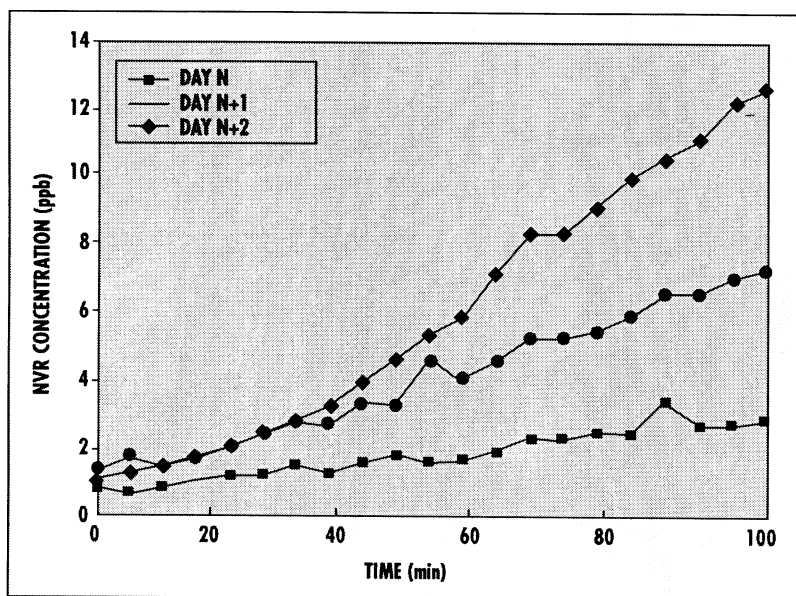
Figure 6: Measurement of colloidal silica leaching from mixed-bed deionizer after daily injections of colloidal silica.

UV because this much shorter wavelength generates highly reactive hydroxyl radicals at the surface of the quartz tubes. The radicals attack the quartz and release dissolved silica. The 254-nm UV wavelength does not have enough energy to generate hydroxyl radicals. The potential of a 185-nm UV wavelength to generate dissolved silica is rarely observed because in nearly all cases an ion-exchange bed is placed immediately after a 185-nm-wavelength UV system and therefore completely removes the dissolved silica almost as soon as it is created.

New Methods for Colloidal Silica Removal

Dissolved silica is much easier to remove than colloidal silica. A potential colloidal silica removal method would there-
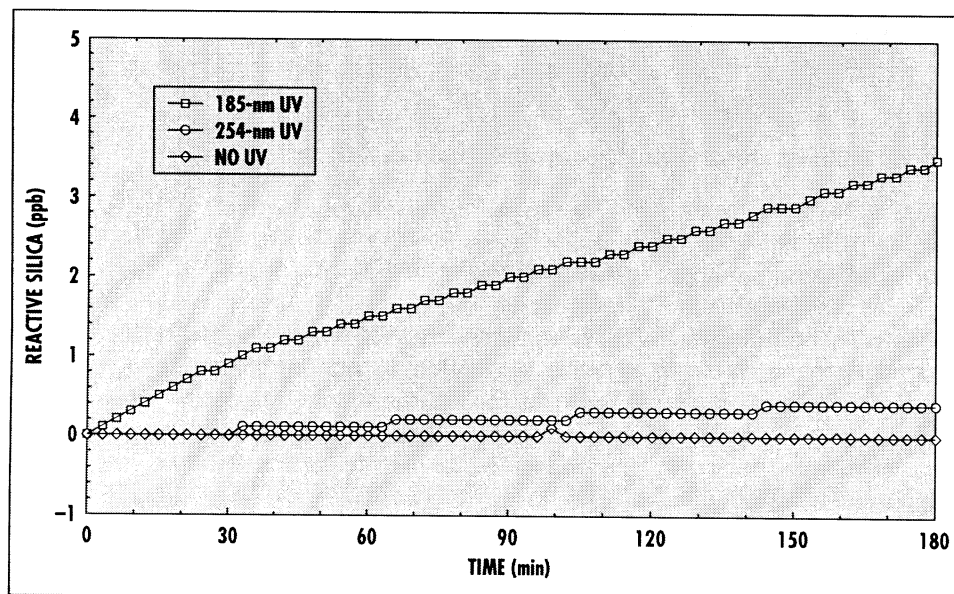
fore be to convert colloidal silica into dissolved silica. As previously stated, a 185-nm UV wavelength generates hydroxyl radicals that attack quartz. Can these hydroxyl radicals also attack colloidal silica? An experiment was performed in which five sizes of colloidal silica—5, 11, 22, 65, and 85 nm—were each sequentially injected for 60 minutes upstream of a 185-nm-wavelength UV system and dissolved silica was monitored downstream by the silica analyzer. The instrument should read background dissolved silica levels unless the colloidal silica is converted to dissolved silica. The downstream silica levels recorded by the analyzer, shown in Figure 8, indicated that, regardless of colloidal silica size, there was no observed increase in dissolved silica. The effect of the previously reported 185-nm radiation dissolving the quartz sleeves has been subtracted from the data shown in Figure 8. We concluded that using 185-nm UV alone cannot convert colloidal silica into dissolved silica.

Knowing that ozone is a powerful oxidant used extensively to control bacteria in water systems, we performed an experiment in which the five sizes of colloidal silica were each sequentially injected for 60 minutes into a UP-water supply with continuous ozone injection at 50 ppb. Once again a silica analyzer measured downstream levels of dissolved silica to see if any colloidal silica was converted to dissolved silica. As Figure 9 shows, there was no observed increase in dissolved silica levels. It is therefore unlikely that ozone is capable of transforming colloidal silica into dissolved silica.

If 185-nm-wavelength UV radiation and ozone cannot be used independently to convert colloidal silica into dissolved silica, is there a possibility that they can be used in combination? An experiment was performed in which the five sizes of colloidal silica and ozone were continuously injected upstream of a 185-nm UV system and dissolved silica levels were measured downstream as before. The results, depicted in Figure 10, indicate a gradual increase in dissolved silica over time, regardless of the initial colloidal silica size. From this result we concluded that the combined use of 185-nm-wavelength UV radiation and ozone converts colloidal silica into dissolved silica.

The combined use of 185-nm-wavelength UV radiation and ozone to dissolve colloidal

Figure 7: Effect of 185- and 254-nm UV radiation on dissolution of silica quartz within the UV system.

silica can be explained by the action of the UV radiation on ozone. Mechanisms have been proposed in which hydroxyl radicals are generated when 185-nm UV wavelength acts on ozone in water.[7,8] The hydroxyl radicals generated by the 185-nm UV system alone probably occur quite close to the surface of the quartz sleeve and do not penetrate very far into the bulk of the water. Because ozone is at a constant level throughout the bulk of the water, the action of the 185-nm UV wavelength on the ozone occurs close to the colloidal silica, so the hydroxyl radicals have a greater opportunity to attack and convert the colloidal silica to dissolved silica.

Figure 8: Effect of 185-nm UV radiation on dissolution of colloidal silica.

Conclusion

The combined use of an on-line dissolved silica monitor and a nonvolatile residue monitor in UP water gives an overall measurement of both dissolved and colloidal silica in near real time. The detection efficiency of the NRM is strongly size dependent; the smaller the particle size, the higher the detection efficiency. However, the NRM has a linear response to increasing concentrations of colloidal silica of the same size. Because the monitor's response is size specific for colloidal silica and nonspecific for other contaminants, it should be used with other instruments to give meaningful quantitative measurements of silica levels in UP water.

Mixed-bed ion-exchange resins effectively remove dissolved silica. Yet these same resins only partially remove colloidal silica and then prematurely release it as the ion-exchange bed becomes exhausted.

The use of 185-nm-wavelength UV radiation generates highly reactive hydroxyl radicals that cause the dissolution of quartz and the subsequent release of dissolved silica into a UP-water system. The combined use of ozone and UV radiation has been shown to convert colloidal silica into dissolved silica because of the generation of hydroxyl radicals close to the colloidal silica.
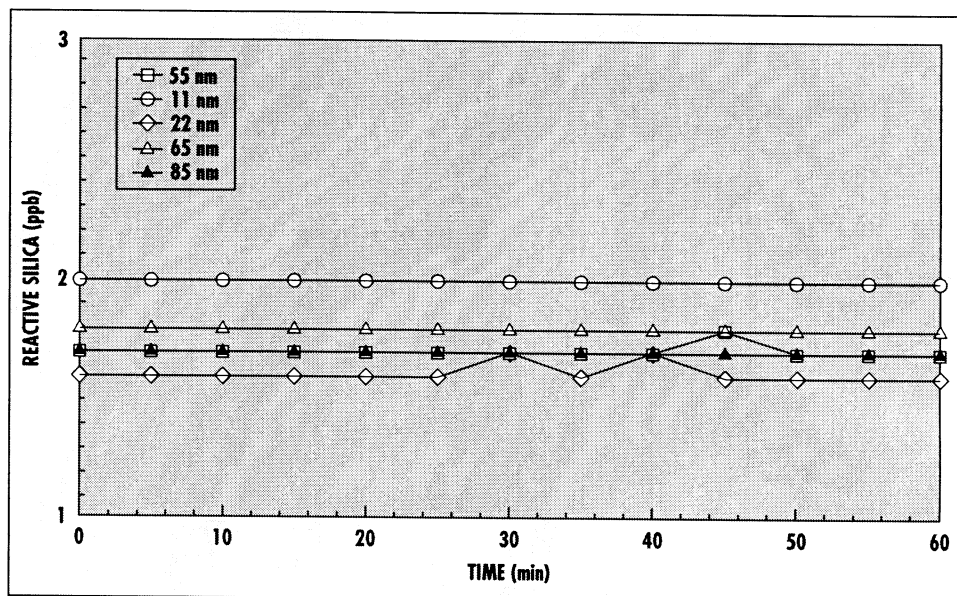

Figure 9: Effect of ozone on dissolution of colloidal silica.

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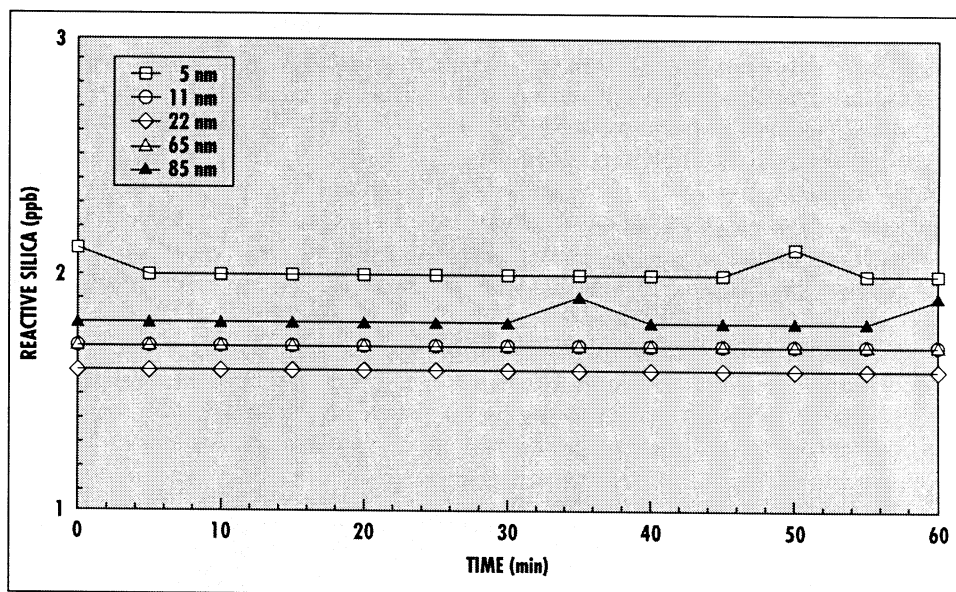
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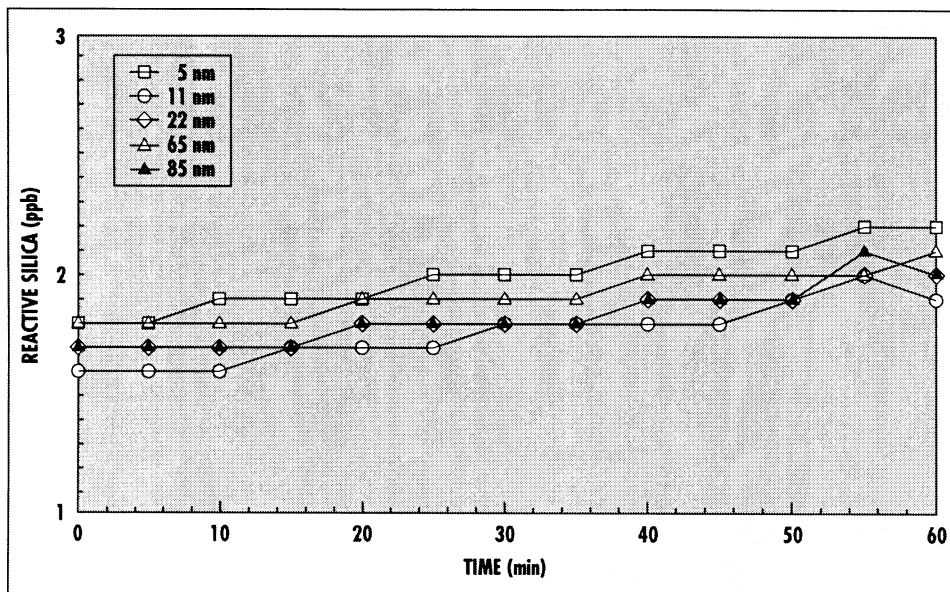
Figure 10: Effect of combined use of ozone and 185-nm UV radiation on dissolution of colloidal silica.

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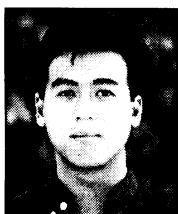
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