

Monitoring Steam Purity in Power Plants

Part 2: Direct Measurement of Contaminants

Part 1 of this application note discussed contaminants typically found in steam and the harm they cause if allowed into the turbine at concentrations above a safe level. It also described how cation and degassed cation conductivity can be used to detect changes in contamination level. Part 2 continues the discussion with respect to the specific contaminants, sodium and silica, for which viable process analyzers are available.

BACKGROUND

Industry guidelines recommend that the steam entering the turbine contain no more than 10 ppb of silica and 2 ppb of sodium. Higher concentrations of either contaminant lead to deposition on turbine surfaces. Silica deposits primarily reduce turbine efficiency by interfering with steam flow, although heavy deposition can also lead to physical damage. Sodium salt deposits present a different hazard. During outages, these deposits become moist and in the presence of oxygen create a highly corrosive local environment on the metal. Eventually pits form that become initiation points for stress corrosion cracking and corrosion fatigue when the turbine returns to operation. An oxygenated environment is not always necessary, however. Sodium hydroxide deposits can induce severe corrosion in the turbine during normal operation when no oxygen is present.

CONTROLLING CONTAMINANTS IN UNITS WITH STEAM DRUMS

Contaminants, including sodium and silica, enter the system primarily through poor quality makeup water and condenser tube leaks. They are carried in the feedwater to the boiler or to the heat recovery steam generator (HRSG), where they accumulate, and a portion carries over with the steam as vapor or in droplets of entrained boiler water. Sodium, in the form of treatment chemicals, trisodium phosphate, disodium phosphate, and sodium hydroxide, is also intentionally added to boilers and HRSGs.

The concentration of sodium and silica in steam, like all contaminants, depends on the concentration in the boiler water. Therefore, steam purity requirements are met by controlling the concentration of dissolved solids in the boiler. Carryover increases as drum pressure rises, so the amount of silica and sodium that can be tolerated decreases with increasing drum pressure.

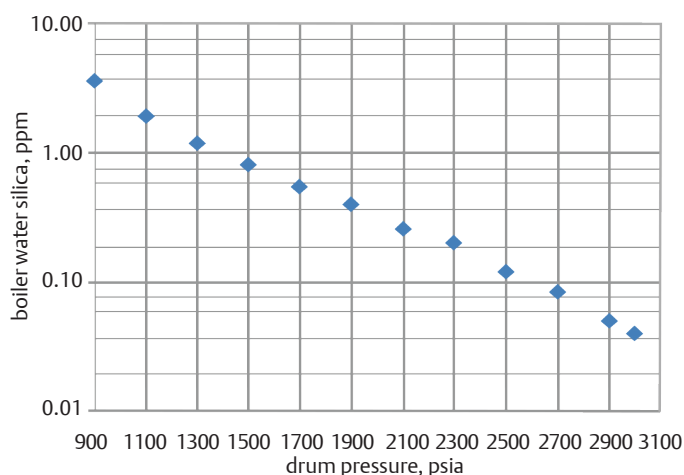
The only way of controlling dissolved solids in boiler water is through blowdown. Because they are mostly ionic, boiler water solids are easily measured using conductivity and blowdown is initiated when the conductivity exceeds the limit for the drum pressure.



Conductivity, however, cannot be used to detect silica as it is an extremely weak acid and very poorly ionized. Therefore, boiler water silica must be measured directly. Blowdown for silica might be necessary even though conductivity is within limits.

Carryover, both vaporous and mechanical, can be predicted from drum pressure. Figure 1 is the control chart for vaporous carryover of silica. It shows the maximum amount of silica allowed in the boiler water to ensure silica in the saturated steam is less than 10 ppb. Similar graphs are available for sodium (as well as chloride and sulfate).

Figure 1 - Boiler water silica control chart for vaporous carryover. Boiler water entrained in saturated steam is likely to make the measured silica greater than predicted from volatilization alone.



CONTROLLING CONTAMINATION IN ONCE-THROUGH UNITS

In once-through supercritical units, a steam-water separation never exists, so all the contamination entering the steam generator is carried with the steam into the turbine. Therefore, contamination must be removed upstream of the steam generator, which is the function of the condensate polishers. Polishers are mixed bed ion exchangers (cation resin and anion resin in a single vessel). They are capable of producing water containing less than 0.1 ppb of sodium — chloride and sulfate levels are similarly low—and less than 2 ppb of silica. However, achieving this level of performance requires utmost attention to operating details. A poorly operated polisher will add contaminants to the condensate.

In addition to removing contamination, polishers also remove the weak bases (ammonia and morpholine) added to the condensate for pH control. Although this seems undesirable because the chemicals have to be reinjected, removing ammonia and morpholine actually helps ensure good removal of sodium in the polisher. In fact, keeping a polisher in service past the point it is no longer removing ammonia or morpholine will result in much of the sodium captured by the resin being released back into the condensate.

PROCESS ANALYZERS FOR SILICA AND SODIUM

Of all the major steam contaminants, sodium, chloride, sulfate, silica, and organic acids, viable process analyzers exist for only silica and sodium.

Silica process analyzers use a technique called colorimetry to measure silica. The analyzer captures a portion of sample from a continuously flowing stream. It adds reagents that react with silica in the sample to form a colored compound. The darkness of the color is directly proportional to the concentration of silica, which is the basis of the measurement. Once the color is fully developed, the analyzer measures the color density and with reference to a calibration curve displays the results. Typically, it takes between 10 and 15 minutes to complete an analysis. The analytical method is well-established and has been used in the laboratory and in process analyzers for many years.

Sodium process analyzers use an ion specific electrode (ISE) to measure sodium. Hydrogen ions interfere, so the sample and standards must be treated with a weak base to raise the pH prior to measurement. Because the base adjusts the pH of the sample and standards to the same value, a pH electrode makes a convenient reference for measuring the ISE voltage. Sodium process analyzers typically measure sodium continuously. Sodium ISEs have been used in process analyzers for many years; however, they are rarely used in the laboratory.

MONITORING SILICA AND SODIUM IN THE STEAM WATER CYCLE

Monitoring practices vary widely. Although industry standards do exist, many plant owners regard them as advisory and tailor their practices to meet individual plant operating experience and philosophy.

Measurements in Steam

Most plants with drum-type boilers or heat recovery steam generators (HRSGs) continuously monitor silica in the steam. There is less consensus about sodium. Some plants monitor sodium continuously, whereas others rely on grab samples or do not measure sodium at all. Instead, they use cation conductivity or degassed cation conductivity. Although cation conductivity measures only anions and not sodium (which is a cation), most plant operators regard cation conductivity as a good measure of overall ionic contamination.

Figure 2 shows the steam system for a plant with a conventional drum-type boiler. Figure 3 is the steam system for a plant with an HRSG. Sodium and silica can be measured in the saturated steam, main steam, or reheat steam (not all plants with HRSGs have reheat steam). Practices vary from plant to plant. Although the measurement is said to be in steam, the actual sample is the condensate produced once the steam has been extracted, cooled, and the pressure reduced.

Figure 2 - Potential sample locations for silica and sodium in the steam from a drum-type boiler. Saturated steam is in equilibrium with boiler water at the boiling point. It is always superheated before being sent to the turbine. Reheat steam is exhaust steam from the high pressure turbine returned to furnace to pick up additional superheat before going to the intermediate and low pressure turbines. Attemperation water is sprayed into the superheater and reheater outlet headers to control the temperature of the steam.

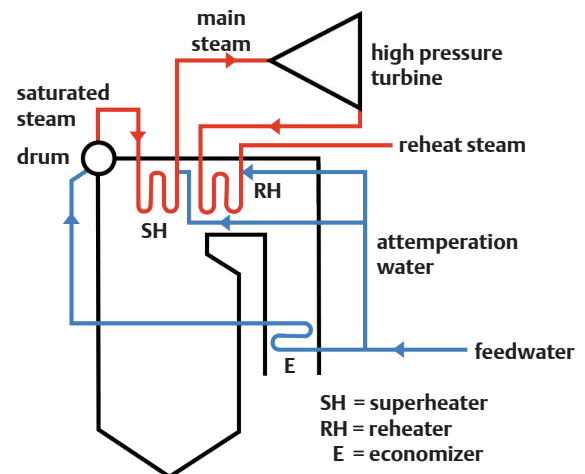
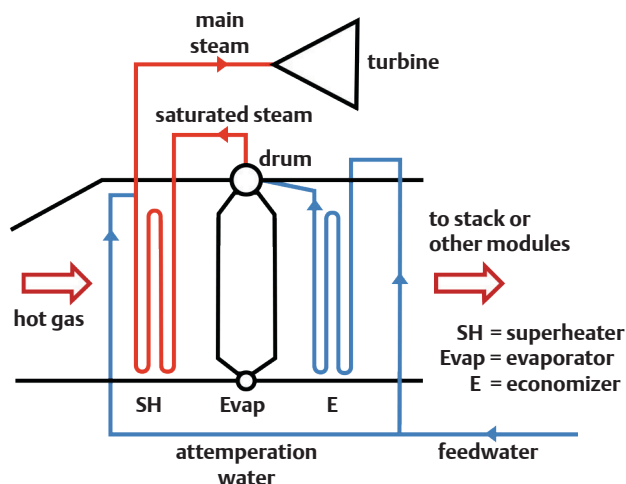


Figure 3 - Potential sample locations for silica and sodium in the steam from a single module in an HRSG. HRSGs usually have two or more modules or pressure sections. Silica and sodium are typically measured only in the steam from modules supplying the turbine.



The contamination level is likely to be slightly different in saturated, superheated, and reheat steam. Two factors are at work. Attenuation water, which allows contaminants in feedwater to bypass the drum, increases contamination. Deposition on the superheater and reheater tubes reduces contamination.

Measurements in Boiler Water

Because the amount of silica and sodium in the steam depends on the concentration in the boiler water, many operators find monitoring boiler water, particularly for silica, is a good way to check the steam analysis for accuracy.

For monitoring silica in steam and boiler water, a dual-stream analyzer, which costs considerably less than two single-stream instruments, is cost-effective. Because dual-stream instruments alternate between samples, the potential exists that an out-of-limits condition in one stream will be undetected while the other stream is being measured. However, silica levels in boiler water and steam do not change rapidly and are closely related, so using a single instrument to measure both samples is not likely to be a problem.

Continuously monitoring sodium in both boiler water and steam is relatively rare. However, if such monitoring is desired, a dual-stream instrument is not recommended. Sodium ISEs are inherently slow to respond to concentration changes. Stabilization time when switching from boiler water (1–3 ppm sodium) to steam (1–2 ppb sodium) can be several hours.

Measurements in Polished Condensate

Nearly all supercritical plants monitor sodium continuously at the polisher. Normally, the polisher plant consists of two, sometimes three, vessels arranged in parallel. Sodium is measured at the outlet of each vessel and in the combined effluent. It is also common to

measure sodium in the unpolished condensate. Unlike boiler water and steam, the difference between sodium levels in the polished and unpolished condensate during normal operation is typically less than an order of magnitude, so the slow response time of the sodium ISE to a large concentration change is not a concern. A multi-stream analyzer is ideal.

There is less consensus about monitoring silica at the polisher. Some plants measure continuously, but others rely on daily or once-a-shift testing of grab samples.

MONITORING MAKEUP WATER

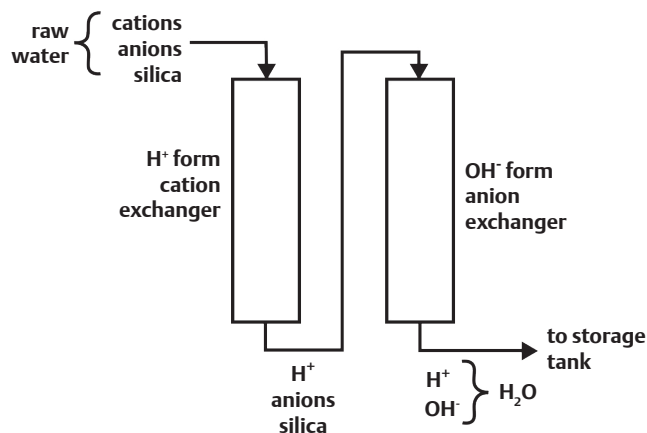
During operation, the plant constantly loses water, which has to be replaced or made up. All plants have demineralizers whose function is to convert raw water into water of sufficient purity for use in the steam-water cycle. Because nearly all the contaminants in the raw water are ionic, conductivity is a simple and inexpensive way to monitor demineralizer performance. Because silica cannot be detected by conductivity, a silica analyzer is also required, and continuous monitoring is common. Continuously monitoring trace sodium in makeup water is unusual, although some plants do measure cation sodium (discussed later).

There are two basic ways to demineralize water, ion exchange and reverse osmosis. Monitoring the performance of both types of demineralizer is discussed below.

Ion Exchange Demineralizers

Figure 4 shows a simple two-bed demineralizer. It consists of a hydrogen-form cation exchanger followed by a hydroxide-form anion exchanger. The first bed removes cations from the raw water, releasing an equivalent amount of hydrogen ions. The second bed removes anions releasing an equivalent amount of hydroxide ions. The anion exchanger also removes silica, although the mechanism may not involve true ion exchange. The hydrogen and hydroxide ions released from the resins neutralize each other, and the result is high purity water.

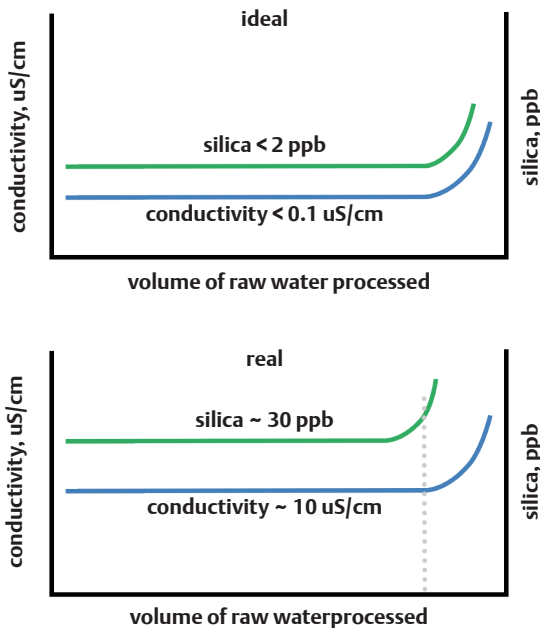
Figure 4 - Ideal two-bed demineralizer.



The upper graph in Figure 5 shows the conductivity and silica in the product water (effluent) from the demineralizer shown in Figure 4 as a function of the volume of water treated assuming ideal behavior. The water quality is excellent and remains that way until the resins become exhausted, i.e., have removed all the cations, anions, and silica they can hold. Then, the conductivity and silica concentration increase in tandem.

The lower graph shows the effluent from a real two-bed demineralizer. The product water is less than perfect. The conductivity during the service run can be as high as 10 uS/cm and the silica 30 ppb or greater. Importantly, at the end of the run, silica appears in the effluent before the conductivity increases. Thus, relying solely on conductivity to trigger removal of the demineralizer from service allows a substantial amount of silica-contaminated water to enter the storage tank and ultimately the system.

Figure 5 - Conductivity and silica concentration as a function of the volume of raw water treated for an ideal (upper graph) and real (lower graph) two-bed demineralizer. The dotted line emphasizes the offset between silica and conductivity at the end of the service run in a real demineralizer.

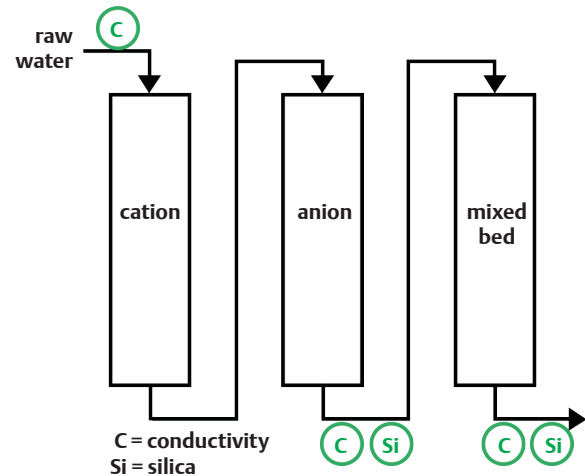


The water produced by a two-bed demineralizer is rarely pure enough for use as makeup. Commonly, a mixed bed exchanger is installed downstream to polish the water, i.e. remove the remaining contamination. Mixed beds used in demineralizers are similar to condensate polishers and can produce high quality water (conductivity < 0.3 uS/cm and silica < 5 ppb).

Figure 6 shows sample points for a cation-anion-mixed bed demineralizer. Silica and conductivity are monitored in both the product water and the anion exchanger effluent. Tracking the anion

exchanger allows the operators to remove the primary beds as soon as they are exhausted. This keeps the contaminant load on the mixed bed low, which improves performance and lengthens its service run. A dual stream silica analyzer is ideal for monitoring the two points. Most operators also measure the conductivity of the raw water as a means of assessing the ion load and predicting the total volume of water that can be processed before the primary exchangers exhaust.

Figure 6 - Recommended sample points for a cation- anion- mixed bed demineralizer. The cation and anion exchangers are the primary ion exchangers and remove most of the contamination. The mixed bed serves as a polisher.



Cation Sodium

Some plants find it useful to measure the sodium leaving the lead cation exchanger. The measurement is commonly called cation sodium.

Ion exchange resins require regular regeneration: treatment with acid and caustic to drive off the captured cations and anions, replacing them with hydrogen and hydroxide ions and restoring the resins to their operating forms. Regeneration is inherently inefficient, so resins are never completely regenerated. It is prohibitively expensive and wasteful to do so. Therefore, regeneration always leaves some resin in the exhausted form, i.e., holding ions other than hydrogen or hydroxide. Significantly, in the lead cation exchanger some resin remains in the sodium form. During operation, cations from the raw water undergo ion exchange, releasing hydrogen ions from the resin. The dilute solution of hydrogen ions is a weak regenerant and forces some of the residual sodium off the resin. The result is a small concentration of sodium (< 5 ppm), called sodium leakage, in the effluent from the primary cation exchanger.

Sodium leakage affects the performance of the downstream anion exchanger. In the anion exchanger, anions are exchanged for hydroxide ions. Because most of the entering anions are paired with a hydrogen ion, the hydroxide is neutralized. However, owing

to sodium leakage, some anions are accompanied by a sodium ion, so the hydroxide is not neutralized and a dilute solution of sodium hydroxide remains. Dilute sodium hydroxide is a weak regenerant and causes leakage, primarily silica, from the anion exchanger. Of course, sodium leaking from the cation exchanger and silica and other anions leaking from the anion exchanger will be removed by the mixed bed. However, high sodium leakage is significant because it increases the load on the mixed bed.

Reverse Osmosis Demineralizers

Reverse osmosis (RO) is also used in demineralizers. RO is a membrane separation technique. Water is pressurized and pushed against a membrane. The membrane allows water (the product water) to pass through it, but blocks most of the dissolved ions and molecules, including silica. Typical rejection is between 98 and 99%, i.e. 1–2% of the dissolved solids pass through the membrane with the product water.

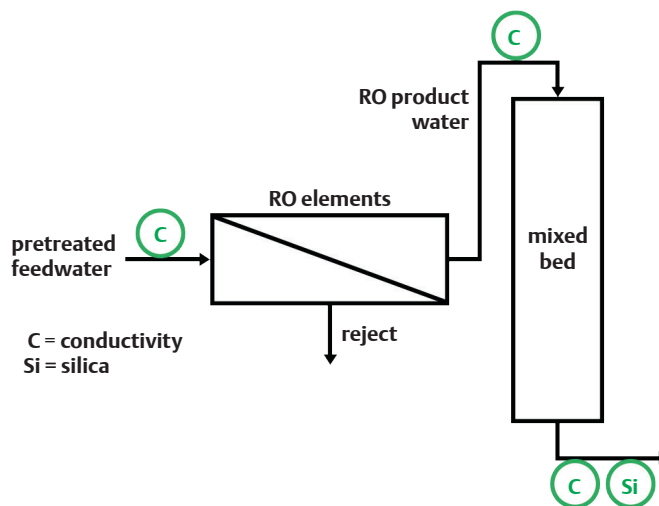
Water quality can be improved by passing the product water through a second RO stage; however, the improvement comes at the expense of yield. In a typical RO stage, about 50% of the entering feedwater is recovered as product, the rest is wasted. If the purified water is sent through a second stage, the overall recovery is about 25%.

Instead of trading diminished yield for better quality water, most RO demineralizer plants simply polish the product water using ion exchange. Mixed bed ion exchange polishers (see above) are commonly used.

Figure 7 shows sample points for an RO-mixed bed demineralizer. Typically, there is no need to continuously monitor silica in the RO product water, and conductivity alone is adequate to detect membrane performance problems. If measuring silica is required, a grab sample is usually sufficient. Both conductivity and silica are continuously measured in the effluent from the mixed bed.

As noted in Figure 7, raw water is always treated before it undergoes reverse osmosis. Pretreatment has several purposes. One is to remove substances that can potentially foul the RO membranes—polymerized (colloidal) silica and high concentrations of dissolved silica are among these. Monitoring silica removal during pretreatment is always through grab sample testing. Silica process analyzers cannot detect polymerized silica, and high concentrations are well above the upper range of the typical instrument.

Figure 7 - Recommended sample points for an RO-mixed bed demineralizer.



SODIUM AND CATION CONDUCTIVITY

Sodium measurements can be used to help identify whether an increase in cation conductivity is the result of increased mineral salt contamination or carbon dioxide in-leakage. (See Part 1 of this application note.) Whether the condenser cooling water is from the ocean, a river, or a lake, or from a recirculating cooling water system, sodium will be a major component. Therefore, an increase in cation conductivity accompanied by an increase in sodium is almost certainly the result of cooling water leakage. Whereas, an increase in cation conductivity without a corresponding increase in sodium is likely the result of increased air in-leakage (or weak acid contamination from some other source).

ANALYZERS

2056 Process Analyzer - Silica

- High accuracy and low detection limit easily meet industry standards for steam purity testing
- 90-day unattended operation.
- Automatic reminder when maintenance is due; no need to keep track of reagent levels.
- Complete diagnostics with troubleshooting guidance available at the press of a button.
- Reduced capital costs; an on-board stream selector allows one analyzer to measure up to six sample streams.



2056 Process Analyzer - Sodium

- Not currently available.

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