

**CATION CONDUCTIVITY MONITORING FOR FASTER START-UPS - A NEW
APPROACH**

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Introduction

In recent years, there has been increased pressure to reduce start-up times for all units, particularly combined cycle units. Most of the combined cycles in the late 1990's were designed to be base loaded due to the low price of natural gas at the time. Increased demand drove the price of natural gas to near \$15 per million BTU's. That, coupled with seasonal demand fluctuations and decreased demand due to the economic recession, has resulted in frequent cycling and start-ups. Combined cycle power stations are more frequently operated in cycling mode. In some cases, this could mean more than 250 start-up and shut-down cycles per year. Combined cycle units designed today have reduced the start-up time by as much as 60%.

Given the substantial fuel cost, environmental issues, and economic impact, any shortening of the time between start-up and reaching full load is of paramount importance. Cation conductivity is still the decisive measurement for the start-up of the steam turbine and the focus is now how fast the cation conductivity results are available and how reliable they are.

The time necessary to obtain correct and representative analysis values is greatly influenced by the design of the sampling and monitoring system. A well designed sampling and monitoring system, coupled with the small staff at a combined cycle plant, can provide significant economic rewards.

Economics of Degassed Cation Conductivity

Today's demands require generating units to rapidly respond to changing generation requirements and supply fluctuations from renewables such as solar and wind power. OEM's have designed combined cycle units that can reach full load in less than 30 minutes without sacrificing efficiency or parts life. To achieve this, the OEM's have incorporated degassed conductivity as their steam purity conductivity requirement. During start-up carbon dioxide (CO₂) is at high concentrations thereby greatly elevating the cation conductivity. CO₂ is not a serious cause for concern for steam turbine corrosion therefore admitting steam to the steam turbine with elevated cation but degassed cation conductivity values within OEM guidelines is acceptable. A well-designed degassed cation conductivity analyzer with precise boiling point temperature control removes 90 – 95 % of the CO₂. Achieving full load one hour sooner will generate additional \$60,000 revenue based on the average price of \$120 per MWH and assuming 500 megawatts of net generation. The average time savings to achieve OEM conductivity limit with DGCC is 3 hours 22 minutes resulting in \$202,000 additional revenue for 500 MW's capacity. Also, degassed conductivity is an excellent tool to determine if elevated cation conductivity is due to CO₂ or more corrosive species such as chloride thereby reducing potential for corrosion and catastrophic failure.

Sampling System

To ensure proper and rapid analysis results the sampling system must be properly designed. A well-designed sampling system conditions samples for the precise measurement of various chemical and physical properties for both grab samples and on-line analysis.

In other words, a properly designed steam and water sampling system preserves the properties of the sample so that analyzers (on-line or laboratory) can provide the most reliable measurements possible.

Sample systems must be able to handle a wide variety of sample temperatures and pressures for both water and steam. The three critical variables to control are temperature, pressure and velocity. The sample should have a high temperature blowdown to remove oxides and other suspended solids. The sample should be cooled prior to reduction of pressure. An automatic temperature shutoff valve should be employed to protect the system should cooling water flow be lost. A filter is typically employed to remove oxides prior to the analyzers. One of the important requirements of sampling system design is the sample flow regulation. A back pressure regulator ensures priority flow to all the analyzers and maintains the flow characteristics of the sample at constant level. The sample then flows to the analyzers and to the grab sample. Figure 1 below illustrates a properly designed sample system.

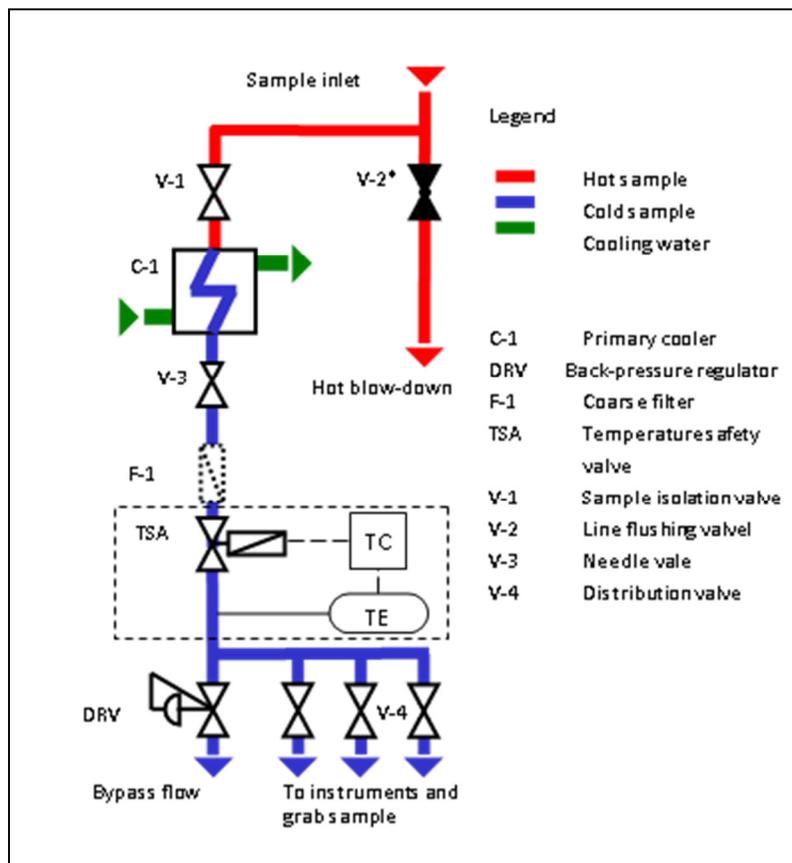


Figure 1: Sample Conditioning System

Start-up Activities

Cation conductivity, often called acid conductivity, remains the critical criterion for start-up of the steam turbine. Industry all-volatile treatment (AVT) steam purity guidelines are listed in Table 1.

Parameter	Cation Cond.	Silica	Sodium	Chloride	Sulfate	Iron	Copper
EPRI	≤0.20*	≤10	≤2	≤2	≤2	-	-
IAPWS	≤0.2	-	≤2	-	-	-	-
GE	≤0.15	≤10	≤3	≤3	≤3	-	-
Siemens	≤0.2	≤20	≤10	-	-	≤20	≤3
Alstom	≤0.2*	≤20	≤10	-	-	≤20	≤1
Toshiba	≤0.3	≤20	≤3	-	-	-	-

Table 1: OEM and Industry Technical Organizations Steam Purity Limits

*Degassed cation conductivity.

It is common for OEM's to establish operating guidelines when chemistry parameters exceed normal operating limits, such as during start-up or commissioning. Table 2 lists Siemens steam purity guidelines.

Parameter	Unit	AL1	AL2	AL3	AL4
Cation Conductivity*	μS·cm ⁻¹	≥0.2<0.35	≥0.35<0.5	≥0.5<1.0	≥1.0
Silica	ppb	≥20<30	≥30<40	≥40<50	≥50
Iron (Total)	ppb	≥20<30	≥30<40	≥40<50	≥50
Copper (Total) ⁽³⁾	ppb	≥3<5	≥5<8	≥8<10	≥10
Sodium ⁽⁴⁾	ppb	≥10<15	≥15<20	≥20<25	≥25
Period per incident	H	≤100	≤24	≤4	0 ⁽²⁾
Accumulated total per year	H	≤2000	≤500	≤80	0 ⁽²⁾

Table 2: VGB guide values for startup and deviation from normal limits for continuous operation.⁽¹⁾

*Continuous measurement at 25°C

AL1 action level 1 AL2 action level 2 AL3 action level 3 AL4 action level 4

- (1) In order to avoid efficiency and lifetime reduction, the turbine startup should preferably occur at values within AL2 or below with a downward trend.
- (2) AL4: steam quality is poor; damage to the turbine cannot be ruled out. The turbine should be shut down.
- (3) Copper content monitoring is not necessary in copper-free systems.
- (4) Sodium monitoring is not mandatory if solid alkalizing agents (caustic or trisodium phosphate) are not applied.

Analyzer Start-up

A considerable amount of time may be required to prepare an instrument for service, obtain a representative sample, and receive an accurate representative analysis result. If the time required preparing the monitoring equipment for operation, acquiring a representative sample, and validating analysis results are taken into consideration, start-up time can be considerably prolonged. Therefore, another feature to help expedite the start-up is the ability to establish flow to the analyzers using demineralized water or condensate, which allows calibration and ensures the analyzers are prepared for operation prior to start-up. Therefore, well designed sampling and monitoring equipment can have considerable influence on start-up times. The following design parameters are critical:

- Sample Availability
 - Optimized sample line design
 - Include a high temperature / high pressure blowdown
 - Employ proper back-pressure regulator
- Analyzer Design Parameters
 - Dimensioning of cation exchanger
 - Use of regenerated and pre-flushed resins
 - Installation of an automatic air vent
- Determination of Conductivity from Corrosive Anions
 - Minimize the contribution of carbon dioxide to cation conductivity

Cation Resin Preparation

It has been shown that regenerated and pre-rinsed resin provides better performance than using new pre-rinsed resin and it provides especially better performance than new non-rinsed resin. Figure 2 illustrates the benefit of new rinsed resin versus new non-rinsed resin.

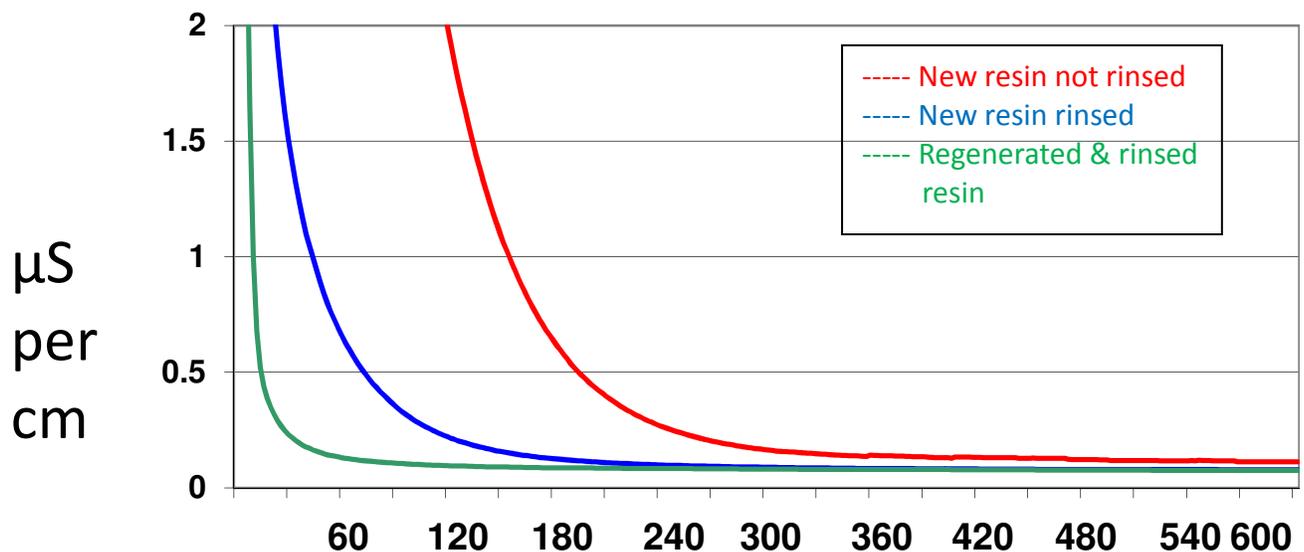


Figure 2: Resin Rinse Time

Air Venting of Cation Exchanger

Another design feature that facilitates unit start-up via obtaining accurate representative analysis results is to remove the air from the cation exchanger to mitigate the influence of carbon dioxide on the resultant cation conductivity. Manual venting is labor intensive, considering the number of monitoring points. With automatic venting, half an hour or more can be saved. Figure 3 illustrates the benefit of automatic air venting the cation exchange vessel to eliminate the influence of carbon dioxide on the cation conductivity.

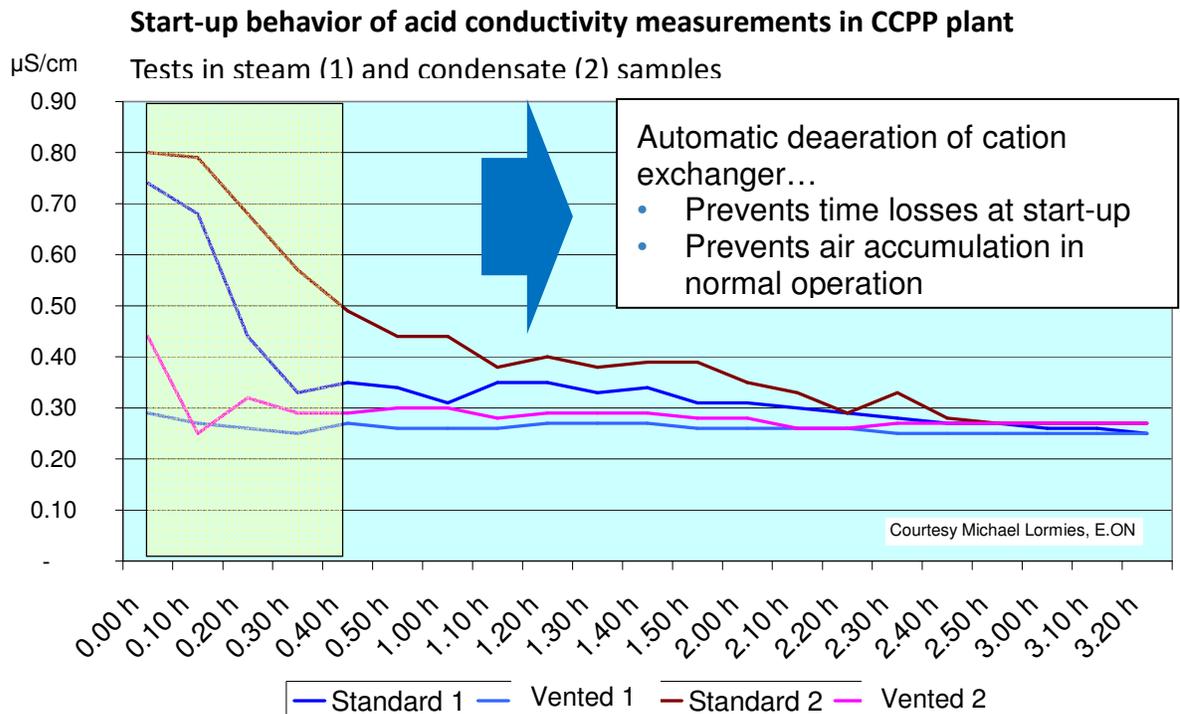
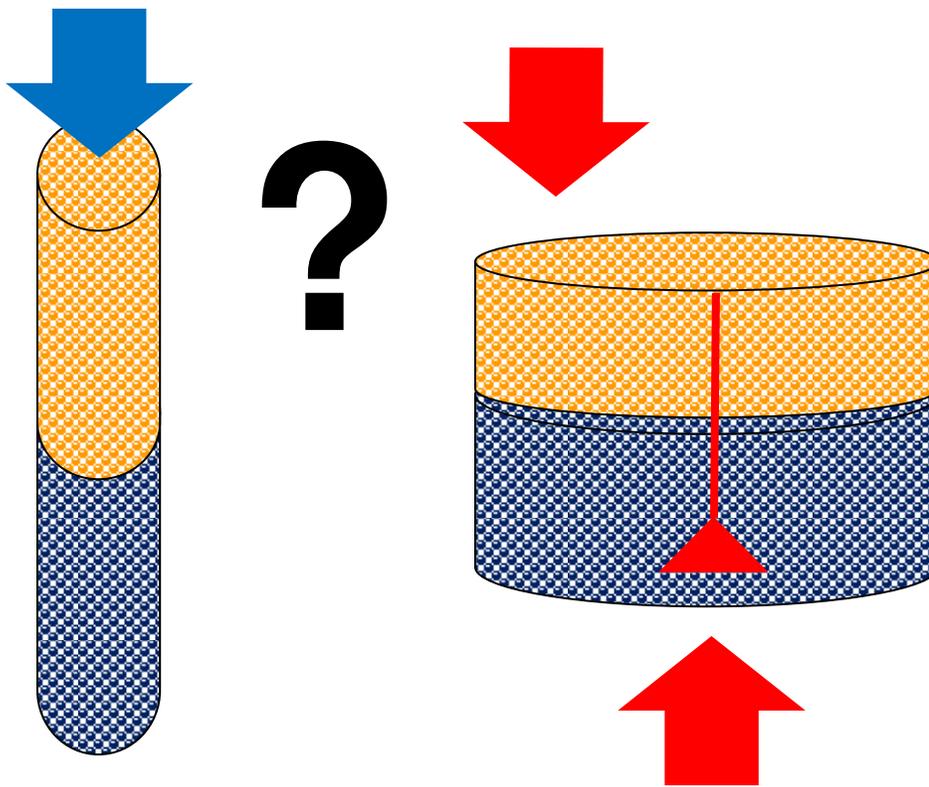


Figure 3: Influence of cation exchanger air venting

1. High pressure steam sample, cold start-up
2. Condensate sample, cold start-up

Cation Exchanger Design Criteria or Dimensioning

The design of the cation exchanger is critical to the performance of the exchanger. The common design is a long and narrow cylindrical tube with the sample entering the top and flowing downward without air venting capability. A more effective design is a liter bottle where the sample flows upward with automatic air venting. Figure 4 illustrates the typical and more effective sample flow through the resin bed.



Typical Flow Path

More Effective Flow Path

Figure 4: Typical and more effective sample flow through resin bed.

Key design criteria are:

- Sample must remain in active resin for ~24s
- Flow from top to bottom
- Automatic air venting
- Diameter / height
- Connections
- Maintenance interval
- Disturbances such as lag time and/or air contamination
- Ease of maintenance

Figure 5 illustrates the flow path of a well design cation exchanger and Figure 6 shows a cation exchanger with a pre-rinse option to have a fresh container of resin rinsed and ready for use when needed.

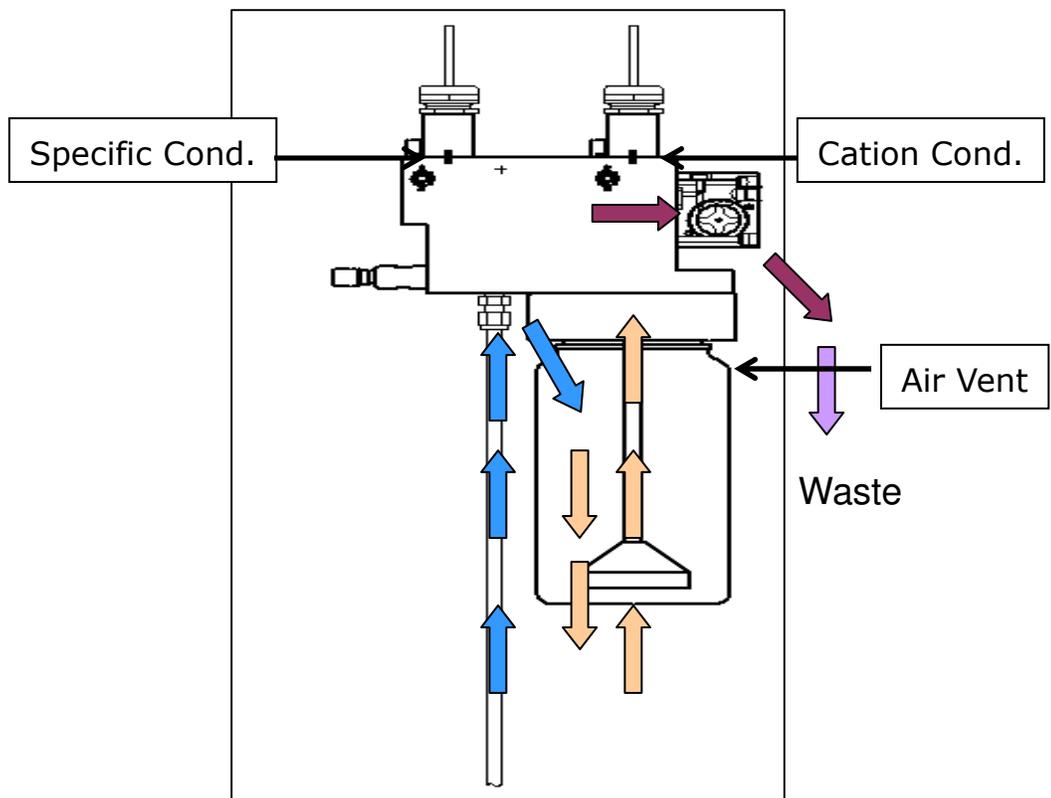


Figure 5: Well designed sample flow through a cation exchanger.

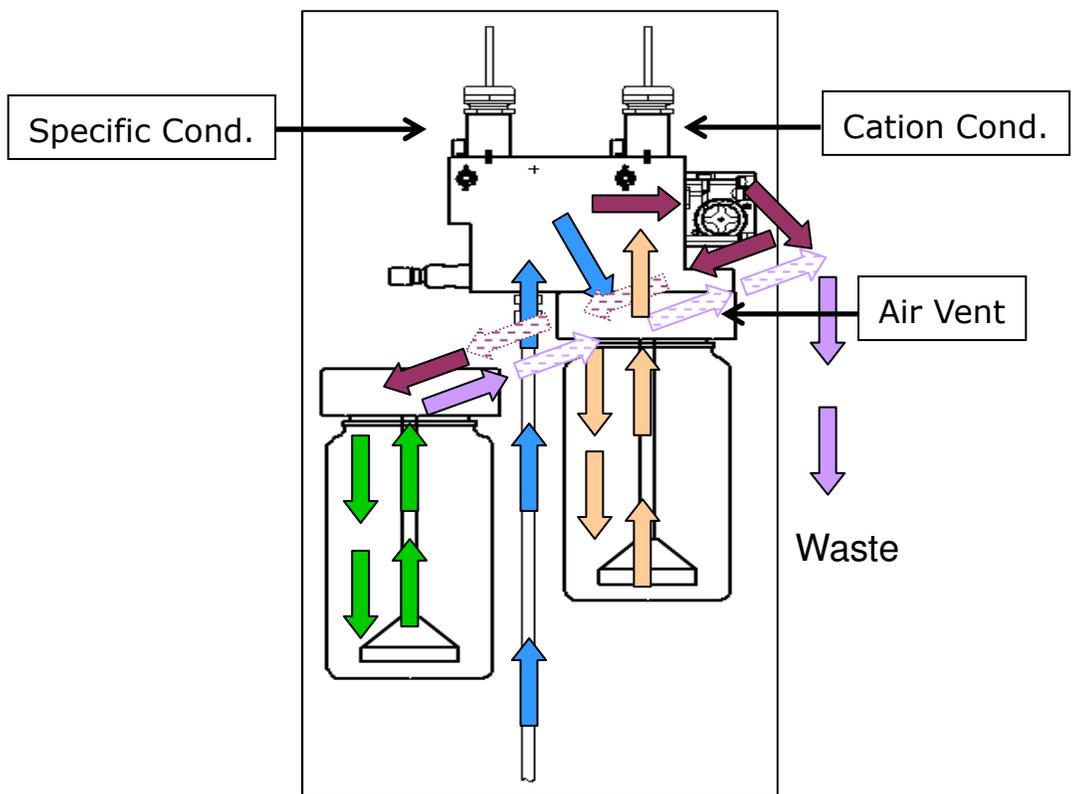


Figure 6: Cation exchanger with pre-rinse option.

The retention time in the cation exchanger should remain in the resin bed for 24 seconds or longer. The liter cation exchanger bottle has 300 milliliters of void space between the resin beads therefore, the residence time in the resin bed, at a flow of 100ml/min, is approximately 3 minutes. This is sufficient time for proper ion exchange. Figure 6 illustrates the lag time in response when injecting 4 ml of 0.01M KCl.

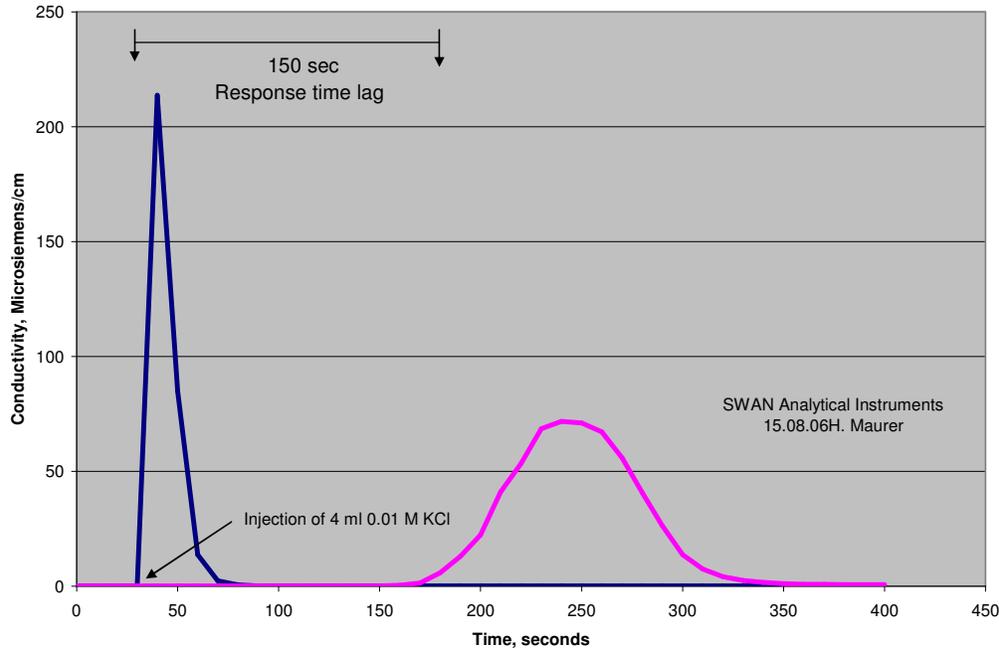


Figure 7: Lag time cation exchanger

Start-up Data

Each OEM has their own steam purity specifications, including allowances for deviation from the normal operating limit for start-ups and commissioning. Values above the normal operating limit may be tolerated for short periods of time, with the greater the deviation, the shorter the allowable duration. These allowances are predicated on the elevated cation conductivity values and are caused by carbon dioxide. This requires credible evidence that the conductivity elevation is indeed due to carbon dioxide and not more corrosive species, such as chlorides, sulfates, and organic acids. The conductivity of a sample is defined by the following algorithm, which is the equivalent conductance of each species multiplied by the concentration of each species.

$$\text{Conductivity} = \lambda H \cdot [H] + \lambda OH \cdot [OH] + \lambda Na \cdot [Na] + \lambda Cl \cdot [Cl] + \lambda CO_2 \cdot [CO_2] + \lambda NH_4 \cdot [NH_4] + \dots$$

$$\lambda x = \text{equivalent conductance} [\mu S \cdot L \cdot cm^{-1} \cdot mol^{-1}]$$

$$[X] = \text{concentration of } X [mol \cdot L^{-1}]$$

Table 3 identifies the common chemical constituents in the sample prior to the cation exchanger, after the cation exchanger, and after the degasser.

Sample upstream of cation exchanger	pH typically > 9.0
Water	H ⁺ , OH ⁻
Contaminants	Na ⁺ , Fe ^{+2&3} , Cl ⁻ , CO ₃ ²⁻ , COO ⁻ , CH ₃ COO ⁻
Alkalizing agent	NH ₄ ⁺
Sample downstream of cation exchanger	pH typically < 7.0
Water	H ⁺ , OH ⁻
Contaminants	Cl ⁻ , CO ₃ ²⁻ , COO ⁻ , CH ₃ COO ⁻
Sample downstream of cation exchanger and degasser	
Water	H ⁺ , OH ⁻
Contaminants	Cl ⁻ , COO ⁻ , CH ₃ COO ⁻ ,

Table 3: Typical species contributing to conductivity

Degassed Cation Conductivity

Most OEM's recognize degassed conductivity for startup and commissioning, and some OEM's specify degassed conductivity as their normal operating guideline. The degassed conductivity unit removes carbon dioxide so the resultant conductivity is a result of more corrosive anions, such as chloride, and organic acids, such as formate and acetate. The degassing process does not remove anions or organic acids, as illustrated in Figure 7. There are typically three methods employed for degassing samples:

1. Nitrogen Sparging
 - a. 70% removal of CO₂
2. Re-boiling
 - a. 28 – 58% removal of CO₂
 - b. 90 - 95% removal of CO₂ with a well-designed system employing precise boiling point temperature control.
3. Membrane
 - a. 40 – 63 % removal of CO₂

Employing degassed conductivity for startup will result in the conductivity value reaching the OEM's limit, allowing steam to be admitted to the steam turbine much sooner than when using non-degassed conductivity. Figure 8 shows the response time of degassed versus non-degassed cation conductivity in a laboratory test. The degassed cation conductivity reached the OEM limit much sooner than non-degassed cation conductivity.

A well designed degassed conductivity monitoring system contains the following features:

1. Measurement based on ASTM D4519-94.
2. Reboiler unit with heating and cooling system made of stainless steel.
3. Degasser electronic controller for reboiler with vapor pressure control.
4. Atmospheric pressure measurement for boiling point compensation.

- a. If the temperature is 0.3°C below the actual boiling point the carbon dioxide removal efficiency decreases from 90 % to 60%.
5. Measurement and display of conductivity, pH, & ammonia.
6. Concentration, sample temperature, and sample flow indication.
7. Calculation of resin consumption with alarm capability.
8. Automatic shutoff of reboiler with loss of flow.
9. Consistently removes 90-95% of carbon dioxide.

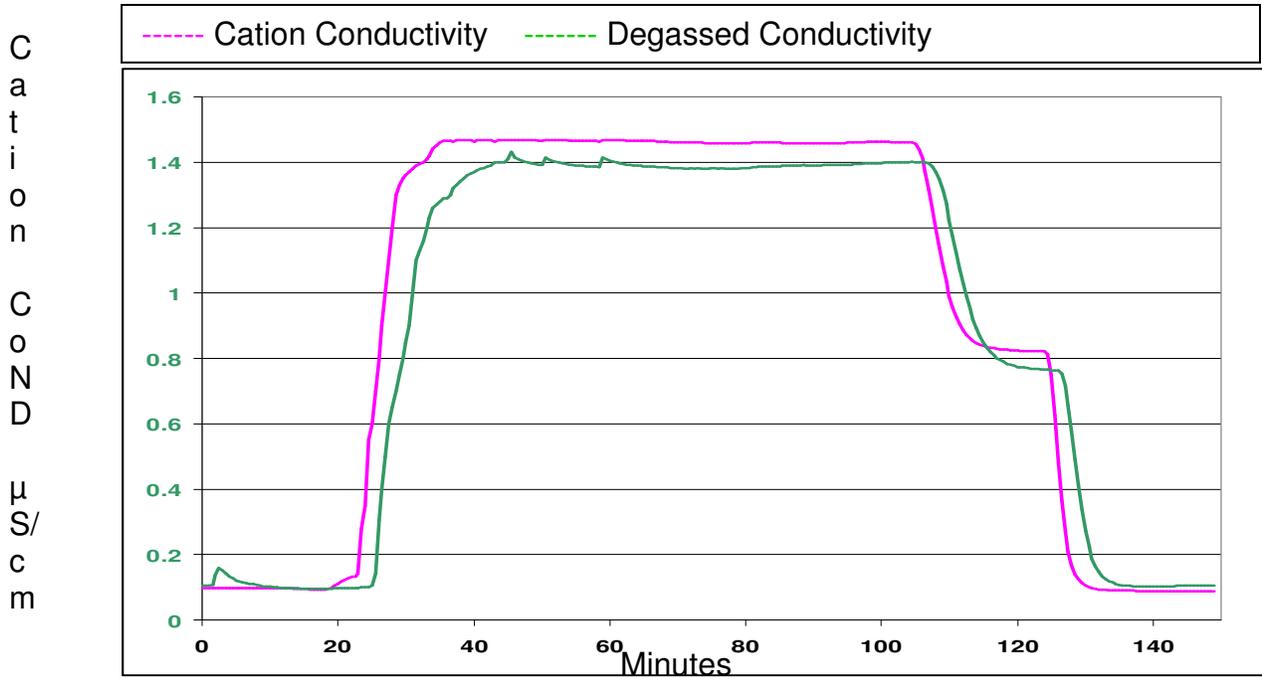


Figure 8: Degassed versus cation conductivity in the presence of acetic acid in two concentrations.

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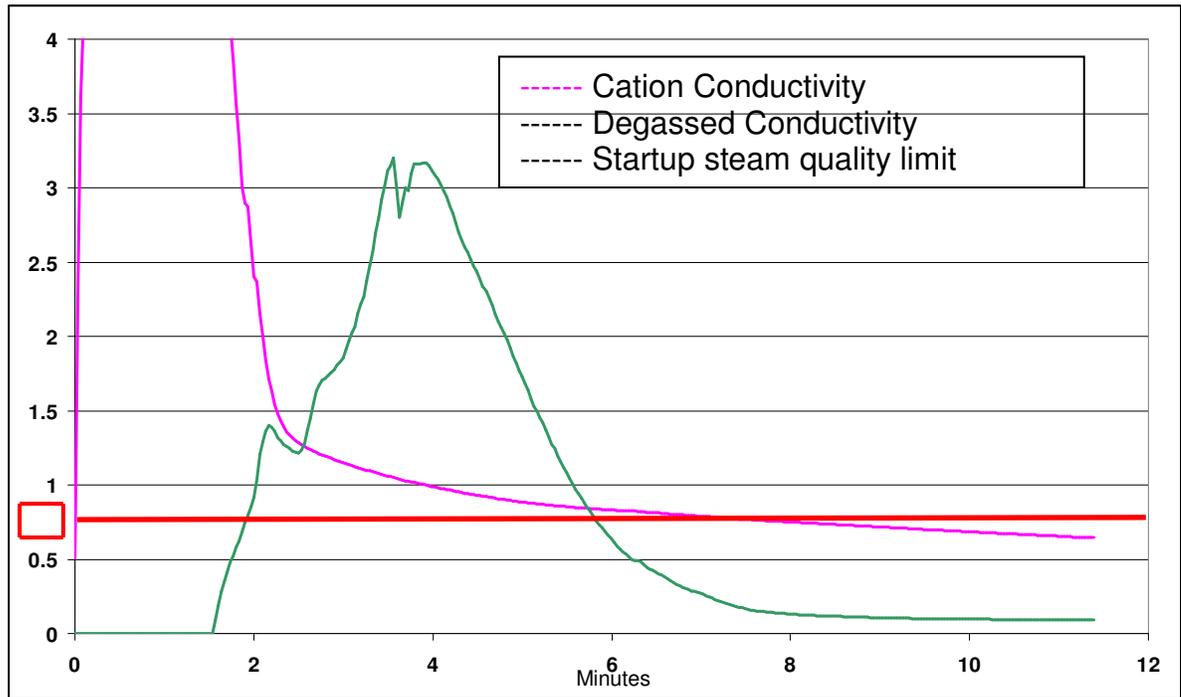
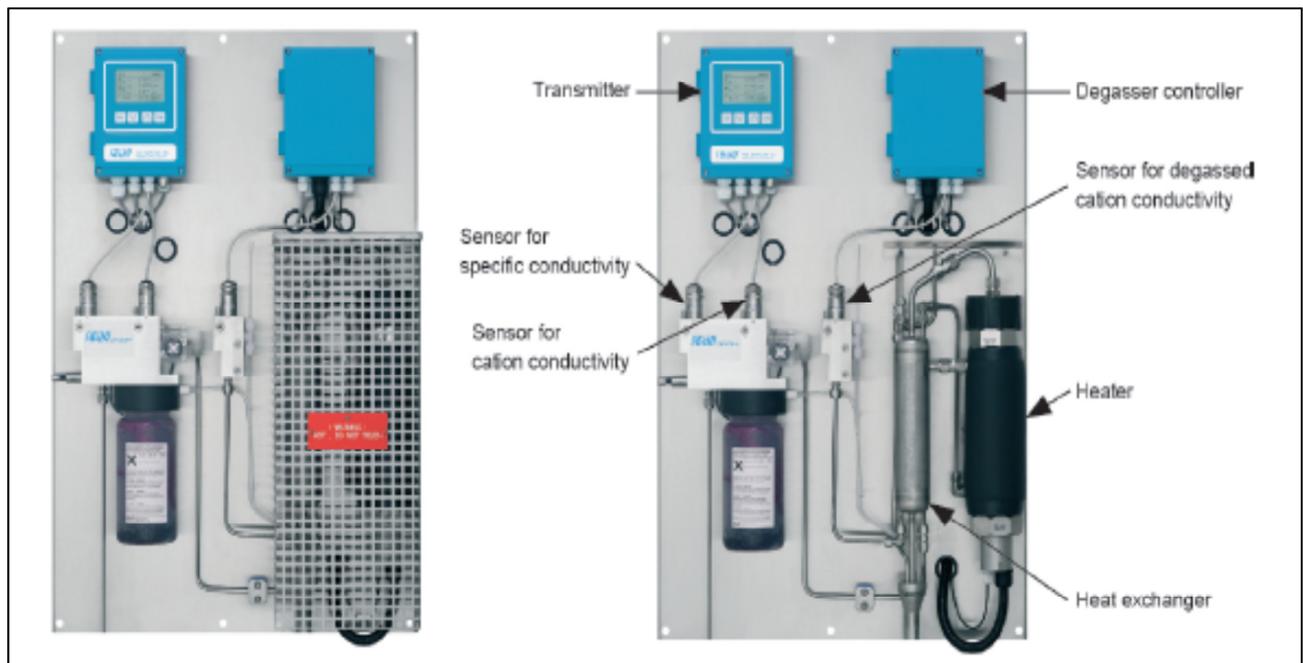


Figure 9: Laboratory illustrating response time of degassed versus non-degassed cation conductivity.

Figure 10 is pictures a number of available degassed conductivity monitors.



Reboiler with Precise Boiling Point Temperature Control



Nitrogen Sparger



Reboiler



Membrane



Reboiler

Figure 10: Degassed Conductivity Monitoring Units Available

Benefits of Degassed Cation Conductivity

The benefits of degassed cation conductivity, as compared to non-degassed cation conductivity are:

1. Removal of less corrosive carbon dioxide, so more corrosive species such as chloride, sulfate, acetate, and formate can be monitored more effectively.
2. Faster startup times.
3. Increased revenues.
4. Reduced startup costs.

Figure 11 compares the degassed cation conductivity versus non-degassed cation conductivity of a triple pressure HRSG. The cycle was treated with ammonia, with the addition of carbonylhydrazide being injected only during startup.

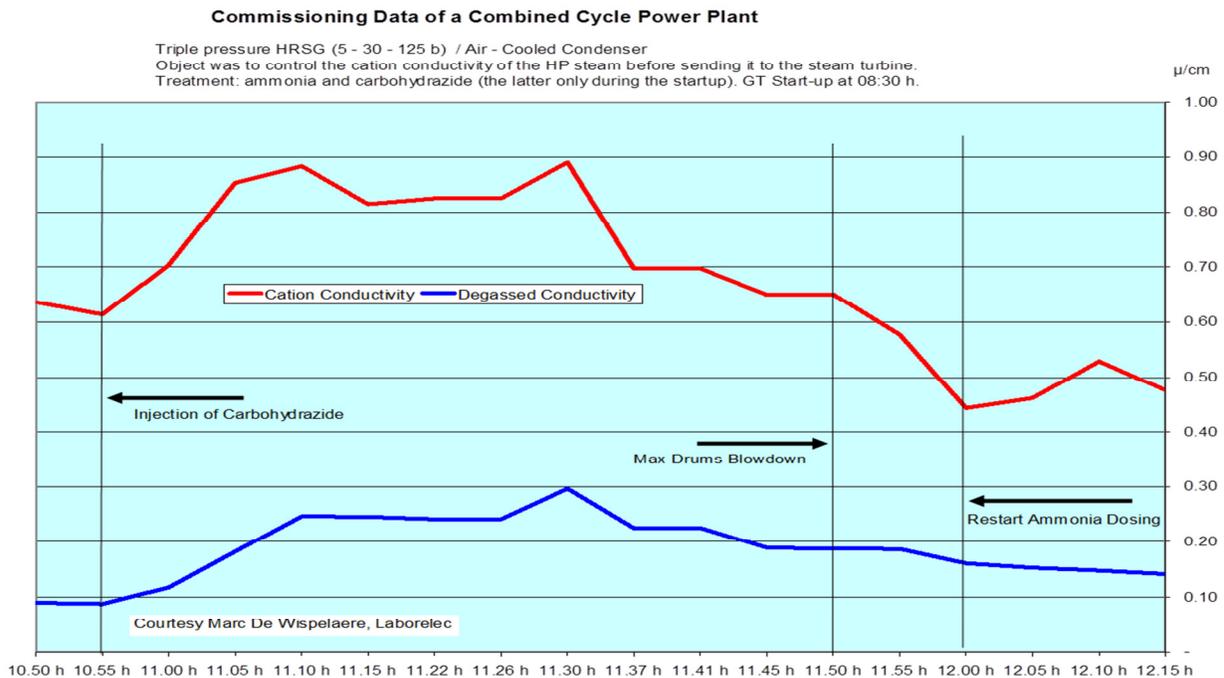


Figure 12: Commissioning data of a triple pressure HRSG; high pressure steam cation versus degassed conductivity.

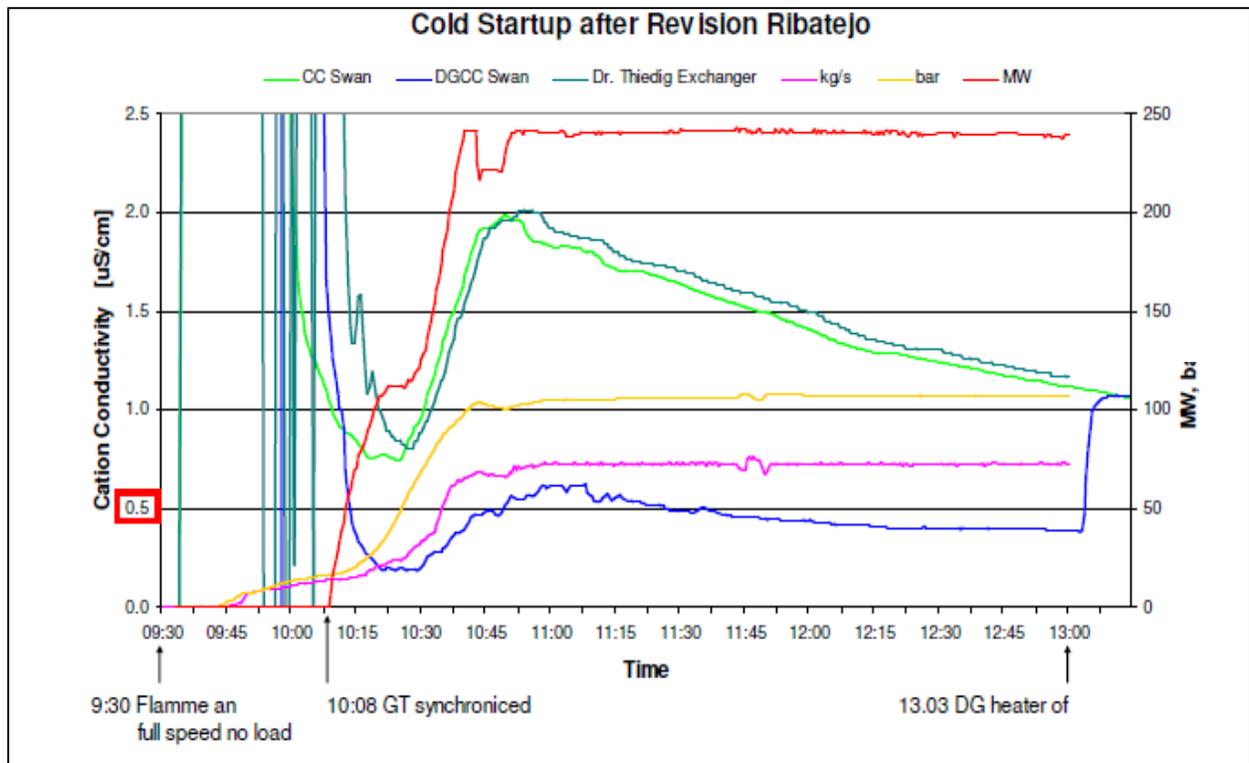


Figure 12: HRSG Cold Startup Data Comparing Cation and Degassed Conductivity

Table 4 illustrates the time savings during cold and warm startups when utilizing degassed conductivity as compared to traditional cation or acid conductivity.

Start	Time from sample flow to DC < 0.5 $\mu\text{S/cm}$	Time from GT start to AC < 0.5 $\mu\text{S/cm}$	Time difference AC/DC < 0.5 $\mu\text{S/cm}$
Cold start # 1	28 min	5h 30min	3h 50min
Cold start # 7	10 min	2h 45min	1h 50min
Cold start # 9	37 min	7h 10min	4h 25min
Warm start # 5	13 min	2h 50min	1h 45min

The time savings for startup and additional revenue generated by admitting steam to the steam turbine much sooner easily justifies the cost of degassed cation conductivity monitoring providing payback with one startup. It is also an excellent trouble shooting tool to determine if elevated cation conductivity is due to carbon dioxide or more corrosive anions such as chloride and sulfate.

Conclusions

Employing the various measures for optimization of continuous monitoring equipment and employing the optimally designed analyzers can reduce the response time of the instrumentation by more than half. Depending on the number of startups per year, a thorough evaluation of the sampling and monitoring instrumentation may provide significant economic rewards. The cost of these improvements are negligible compared to the benefits of reducing the time operating in by-pass mode.

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