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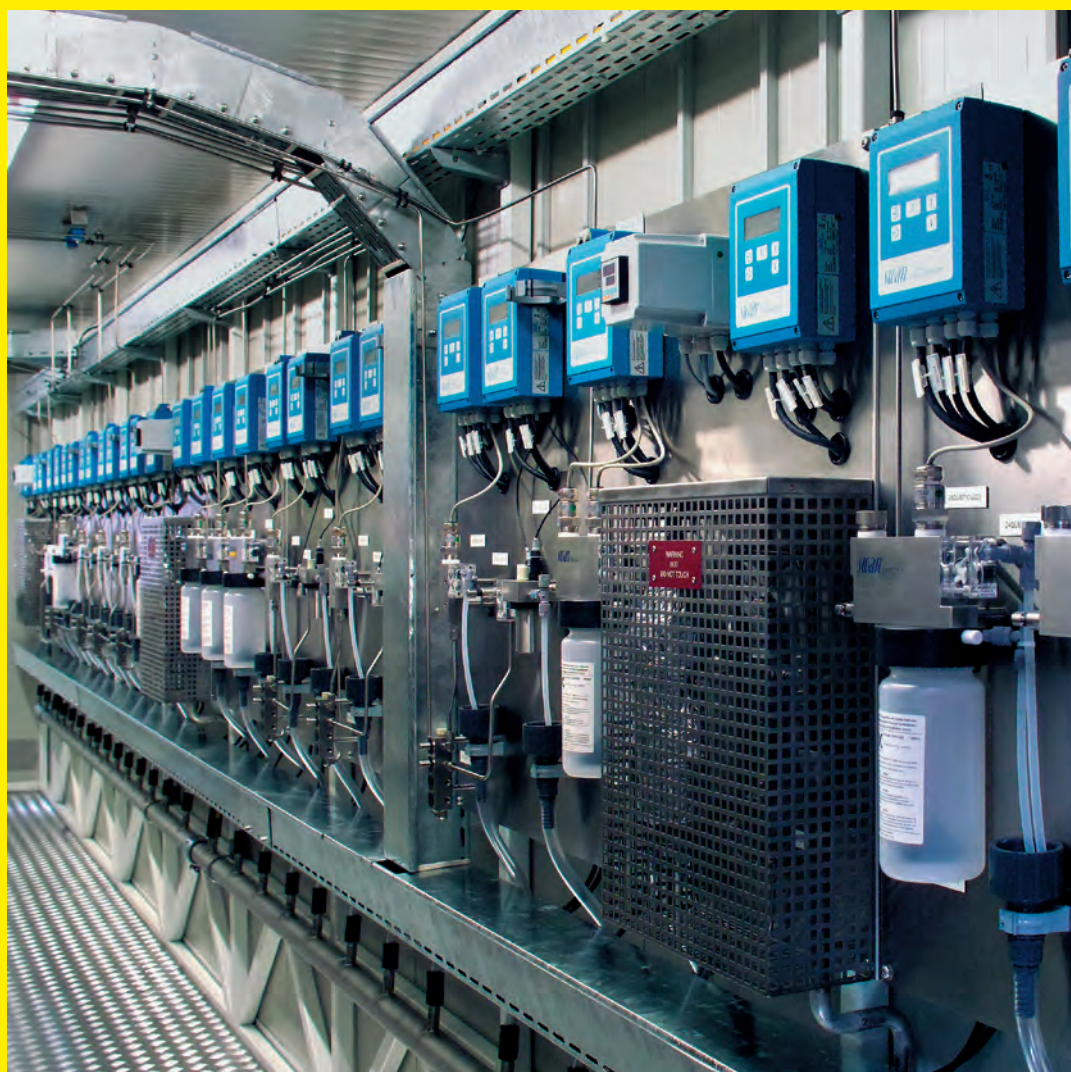
Cation Conductivity Monitoring during Startup

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ABSTRACT

In recent years, the requirements on startup time durations of combined cycle units with heat recovery steam generators have become extreme. In this context, measures taken in the area of monitoring of the key cycle chemistry parameters towards reducing the time necessary to obtain correct and representative analysis values are very important. This paper describes some recent developments and clearly demonstrates that the response time of the instrumentation may be reduced by more than half. In this way, the bypass operation time may be markedly reduced, yielding significant benefits.

INTRODUCTION

In recent years, the requirements on startup time durations of combined cycle units with heat recovery steam generators (HRSGs) have become much more extreme. Due to the liberalization of the power market, combined cycle units are more frequently operated in cycling mode. In this operation mode, units may be started and shut down daily (≥ 250 starts per year). Considering the substantial fuel costs and environmental aspects, any shortening of the time between startup and reaching full load is very important – each individual minute carries weight. *Figure 1* is a comparison of the combined cycle power plant startup times between the late 1990s and 2007.

A comparison of startup times of a combined cycle unit designed for base-load operation (older design) and a current combined cycle unit reveals that the startup time up to full load has been reduced to about 40 % (*Figure 2*). This makes the work of plant chemists very difficult: there is very little time to implement measuring devices and for a plausibility check of monitoring results. It is imperative to reappraise the chemist's working methods and to adapt to new demand.

ACTIVITIES DURING STARTUP

Cation conductivity (called acid conductivity in [1]) is still the decisive criterion for startup of a steam turbine. *Table 1* shows the guideline values for the steam quality during startup of a turbine [2]. As a rule of thumb, the cation conductivity of the steam should be less than $0.5 \mu\text{S} \cdot \text{cm}^{-1}$ with a recognizable downward tendency.

The decisive factors are how fast the cation conductivity value of the steam is available and how correct this value is (the plausibility check). If the period required for the preparation of the monitoring equipment, sample availability included, is considered in the context of the time necessary for the startup of the turbine (*Figure 3*), it is clear that the preparation of the measurement and the plausibility check may considerably prolong the startup procedure.

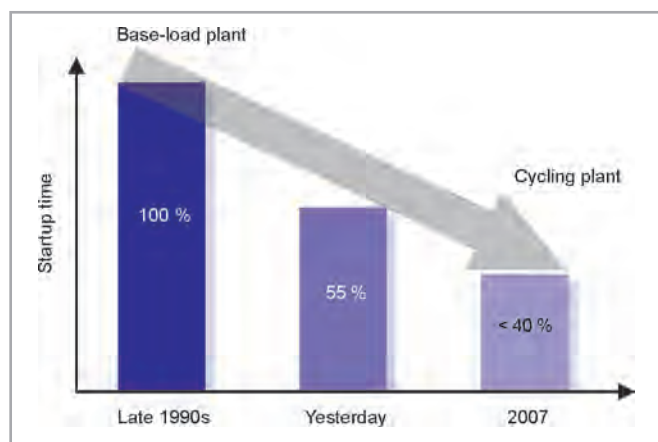


Figure 1: Reduction in combined cycle unit startup time (values for a 400 MW single-shaft cycling unit).

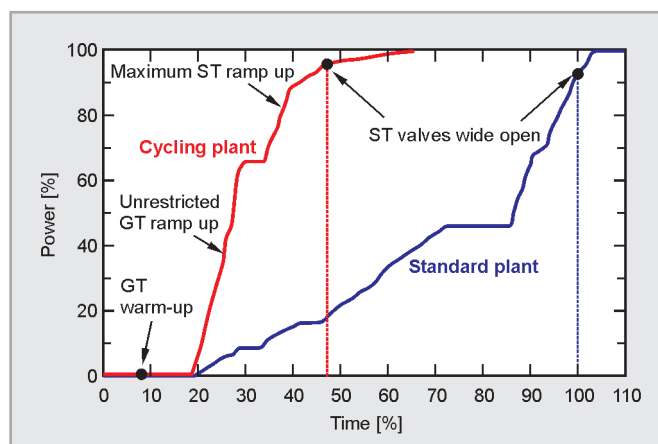


Figure 2: Unrestricted gas turbine startup and maximum steam turbine load ramp – a comparison of a standard and a cycling plant.

GT gas turbine ST steam turbine

Parameter	Unit	AL1	AL2	AL3	AL4
Cation conductivity *	$\mu\text{S} \cdot \text{cm}^{-1}$	$\geq 0.2 < 0.35$	$\geq 0.35 < 0.5$	$\geq 0.5 < 1.0$	≥ 1.0
Silica	$\text{mg} \cdot \text{kg}^{-1}$	$\geq 0.020 < 0.030$	$\geq 0.030 < 0.040$	$\geq 0.040 < 0.050$	≥ 0.5
Iron (total)	$\text{mg} \cdot \text{kg}^{-1}$	$\geq 0.020 < 0.030$	$\geq 0.030 < 0.040$	$\geq 0.040 < 0.050$	≥ 0.5
Copper (total) ⁽³⁾	$\text{mg} \cdot \text{kg}^{-1}$	$\geq 0.003 < 0.005$	$\geq 0.005 < 0.008$	$\geq 0.008 < 0.010$	≥ 0.010
Sodium ⁽⁴⁾	$\text{mg} \cdot \text{kg}^{-1}$	$\geq 0.010 < 0.015$	$\geq 0.015 < 0.020$	$\geq 0.020 < 0.025$	≥ 0.25
Period per incident during which the turbine may be further operated	h	≤ 100	≤ 24	≤ 4	0 ⁽²⁾
Accumulated total period per year	h per year	$\leq 2\,000$	≤ 500	≤ 80	0 ⁽²⁾

Table 1: Guide values valid exclusively for startup ⁽¹⁾ and deviation from the values recommended for continuous operation. Generally: if one individual parameter of a particular action level reaches or exceeds the value stated, the next action level applies.

* continuous measurement at the sampling point 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 of $> \text{AL2}$ with a downward tendency.
- (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.

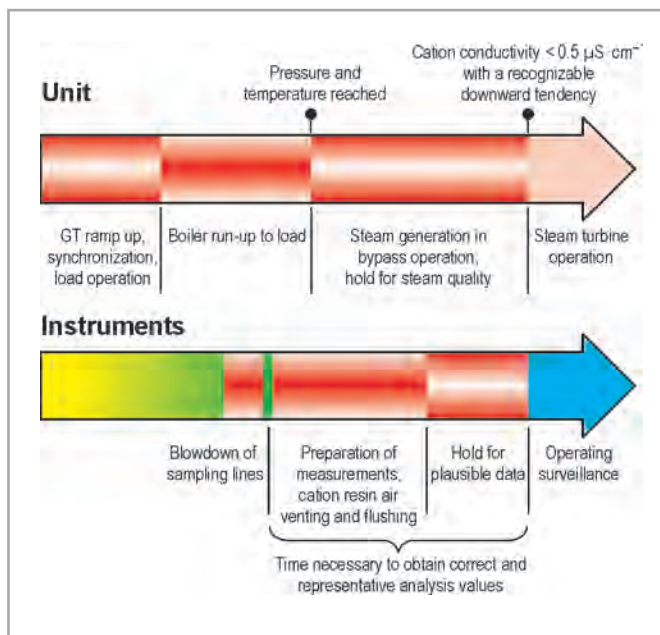


Figure 3: Startup of the unit and expenditure of time for a reliable cation conductivity measurement.

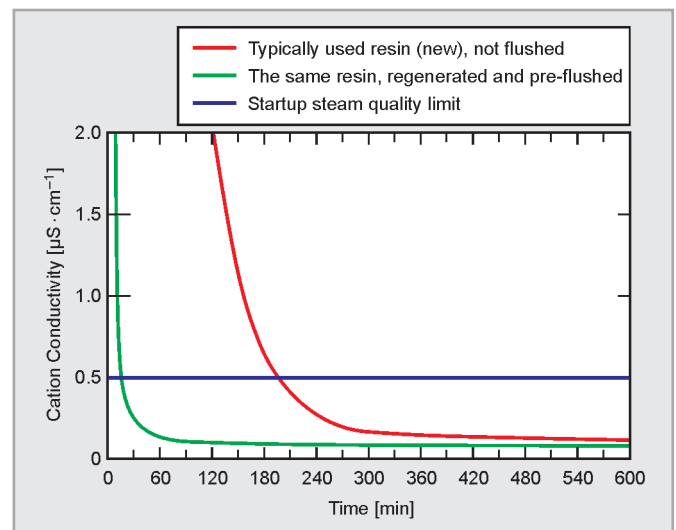


Figure 4: Influence of cation resin quality (courtesy of H. Maurer).

Sample conductivity $0.057 \mu\text{S} \cdot \text{cm}^{-1}$;
resin volume 1 L; sample flow velocity $6 \text{L} \cdot \text{h}^{-1}$;
degasser temperature $99.3 \text{ }^\circ\text{C}$.

PUTTING MONITORS INTO OPERATION

Optimization of the Monitoring Equipment

A closer inspection reveals that the time necessary to obtain correct and representative analysis values may be considerably influenced by skilled design of the monitoring equipment:

- Sample Availability
 - Optimization of the sampling line
 - Installation of high-pressure blowdown valves
 - Application of back-pressure regulators
- Readiness for Service
 - Dimensioning of the cation filter
 - Use of regenerated and pre-flushed resins
 - Installation of an automatic air vent

- Avoidance of Incorrect Results
 - Minimization of the contribution of carbon dioxide to cation conductivity

Use of Regenerated and Pre-flushed Resins Each individual measure contributes to the acceleration of the monitoring activity. *Figure 4* demonstrates the optimum monitoring results with regenerated and pre-flushed resins in comparison to new non-pre-flushed resins. The use of a regenerated and pre-flushed resin may result in a time savings of more than 1 hour. If non-regenerated resins are to be used, focus must be on their cleanliness, and a separate device for resin flushing is required.

Air Venting of the Resin Column Manual air venting of cation resin columns is a particularly laborious activity, which has to be performed on the spot, thus tying down the staff. *Figure 5* shows that more than half an hour may be saved using automatic air-venting devices.

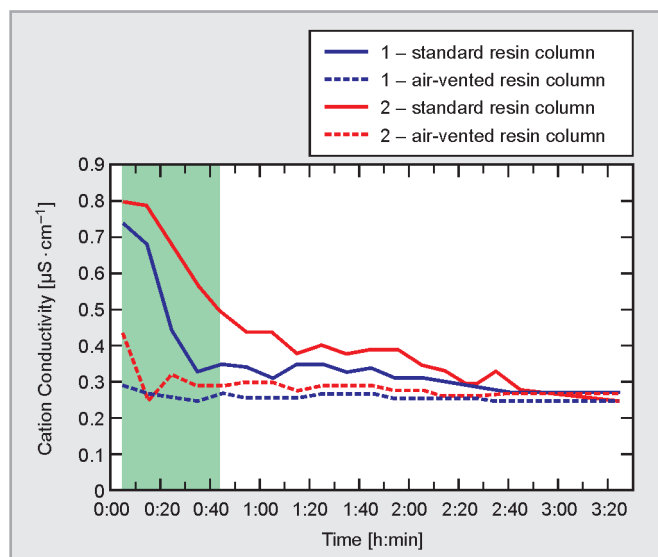


Figure 5: Influence of cation column air venting (courtesy of M. Lormies).

- 1 Combined cycle, high-pressure steam sample, cold startup.
- 2 Combined cycle, condensate sample.

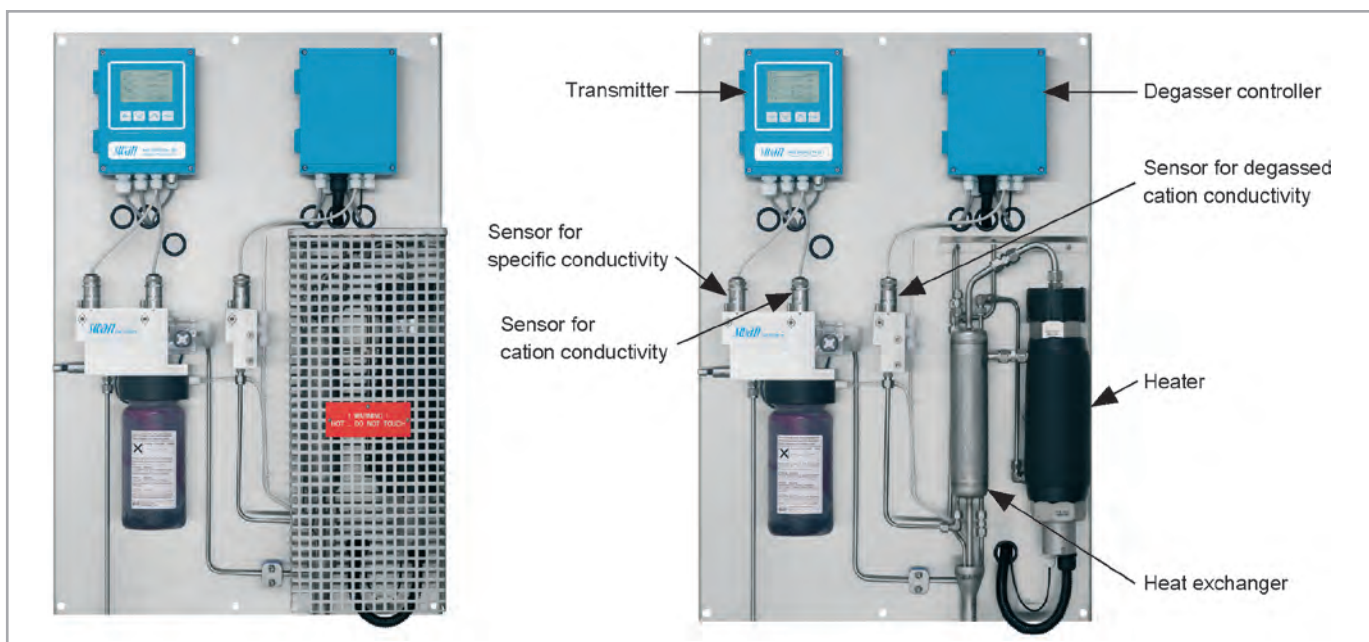


Figure 6: Degassed cation conductivity monitoring system.

Importance of the Data Measured

As already stated, the cation conductivity of the steam should be less than $0.5 \mu\text{S} \cdot \text{cm}^{-1}$ with a recognizable downward tendency. Higher values may be tolerated for short periods of time and during startup provided that they are caused exclusively by carbon dioxide. However, credible evidence must be provided that the increased cation conductivity is actually caused by carbon dioxide and not by dangerous steam contaminants such as chlorides or organic acids. *Table 2* specifies the contribution of water, contaminants and alkalizing agents during the cation conductivity measurement.

Elimination of the carbon dioxide contribution is possible via thermal degassing of the sample. For a reliable measurement, the reproducibility of this procedure is of immense importance. The degassing temperature has to be close to the boiling point at the current air pressure. Identical measuring devices operating at identical temperatures allow for comparison and interpretation of the measured values. A degassed cation conductivity monitoring system is shown in *Figure 6*.

Under no circumstances may contaminants other than carbon dioxide or its species be removed from the sample.

Sample upstream of the cation exchanger	pH typically > 9
Water	H ⁺ , OH ⁻
Contaminants	Na ⁺ , Cl ⁻ , CO ₃ ²⁻ , COO ⁻ , CH ₃ COO ⁻ , ...
Alkalizing agents	NH ₄ ⁺
Sample downstream of the cation exchanger	pH typically < 7
Water	H ⁺ , OH ⁻
Contaminants	Cl ⁻ , CO ₃ ²⁻ , COO ⁻ , CH ₃ COO ⁻ , ...
Sample downstream of the cation exchanger and degasser	
Water	H ⁺ , OH ⁻
Contaminants	Cl ⁻ , COO ⁻ , CH ₃ COO ⁻ , ...
Conductivity $LF = A_H \cdot [H] + A_{OH} \cdot [OH] + A_{Na} \cdot [Na] + A_{Cl} \cdot [Cl] + A_{NH_4} \cdot [NH_4] + \dots \quad [\mu S \cdot cm^{-1}]$ $A_X \quad \text{equivalent conductance } [\mu S \cdot L \cdot cm^{-1} \cdot mol^{-1}]$ $[X] \quad \text{concentration of X } [mol \cdot L^{-1}]$	

Table 2: Sample chemistry – contribution of individual components to conductivity, cation conductivity, and degassed cation conductivity.

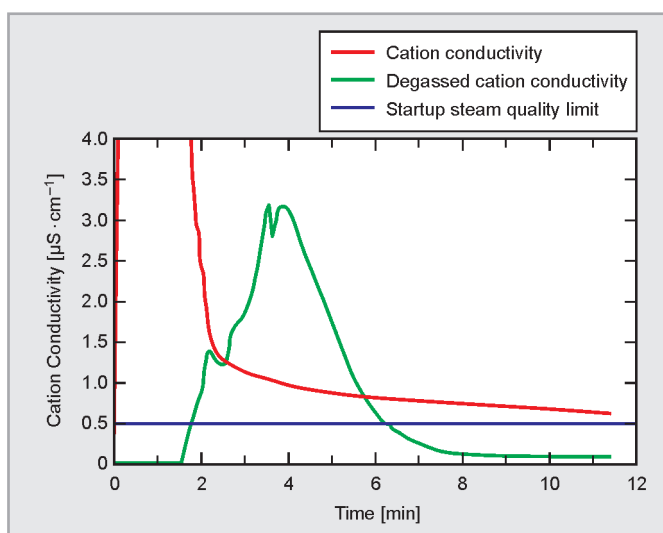


Figure 7: Degassing of the sample in the presence of carbon dioxide (lab experiments).

Sample contains carbon dioxide;
 sample pH 9.8; resin volume 1 L;
 sample flow velocity 10 L · h⁻¹;
 degasser temperature 99.3 °C.

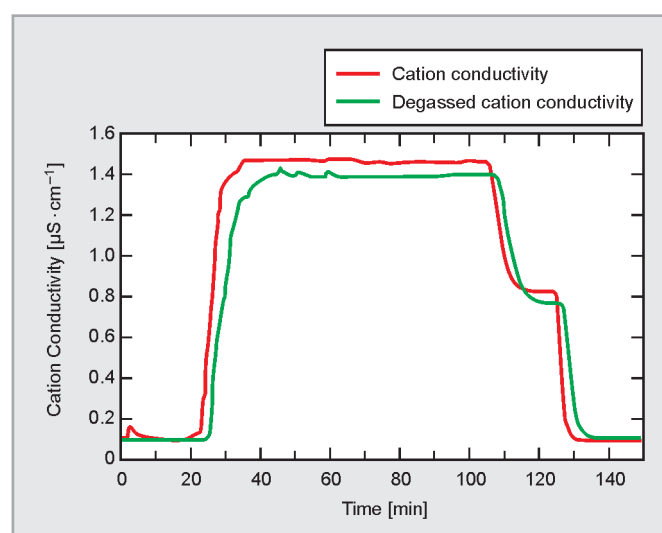


Figure 8: Degassing of the sample in the presence of acetic acid in two concentrations (lab experiments).

Sample pH about 7.0; resin volume 1 L;
 sample flow velocity 10 L · h⁻¹;
 degasser temperature 99.3 °C.

Contaminants in the form of acids (e.g., hydrochloric, sulfuric, formic, acetic acid) must remain in the degassed sample and be measured by the conductivity measurement. *Figure 7* shows the time-dependent behavior of the degassing device (comparison of the degassed and non-degassed cation conductivity in the presence of carbon dioxide). It reveals that carbon dioxide is almost completely removed from the sample. In contrast, *Figure 8* confirms that acetic acid is not removed from the sample during degassing. The small difference between the cation and degassed cation conductivity indicates the presence of carbon dioxide in the sample.

Using the degassed cation conductivity system it is possible to reliably determine whether an increased cation conductivity can be tolerated for a short time or if a risk of undesirable contamination exists. *Figure 9* shows actual operation data. It clearly demonstrates that during the startup of a combined cycle power plant – while the cation conductivity reading is higher than the tolerable value of 0.5 μS · cm⁻¹ for more than one hour – the degassed cation conductivity remains below 0.5 μS · cm⁻¹. It should be noted that the data shown in *Figure 9* was measured during injection of carbonylhydrazide in the startup period.

CONCLUSIONS

When the contributions of the different measures for the optimization of the monitoring equipment are added up, the response time of the instrumentation may be reduced by more than half. Depending on the number of starts per year, a thorough evaluation of the sampling systems and the instrumentation may pay off. The expenditures required for the improvement of these systems are negligible in comparison to the benefits from the reduction in the bypass operation time.

ACKNOWLEDGMENT

The data provided by Michael Lormies (E.ON, Germany), Marc De Wispelaere (Loborelec, Belgium), and Heini Maurer (Swan Analytical Instruments, Switzerland) is greatly appreciated.

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- [2] *Steam Turbine Manual*, 2001. Siemens AG, Erlangen, Germany.

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THE AUTHORS

Michael Rziha is the leader of the department Plant Cleaning and Chemistry at Siemens Power Generation, which is responsible for the entire chemistry of power plants during erection and commissioning, as well as for chemical cleaning and steam cleaning concepts. Previously he worked 10 years as a chemical commissioning engineer and was involved in several projects (nuclear and fossil) worldwide during their commissioning periods. Before taking over the department Plant Cleaning and Chemistry, he worked for 3 years in the design department of Siemens Power Generation (formerly KWU), designing water treatment plants and power plant chemistry.

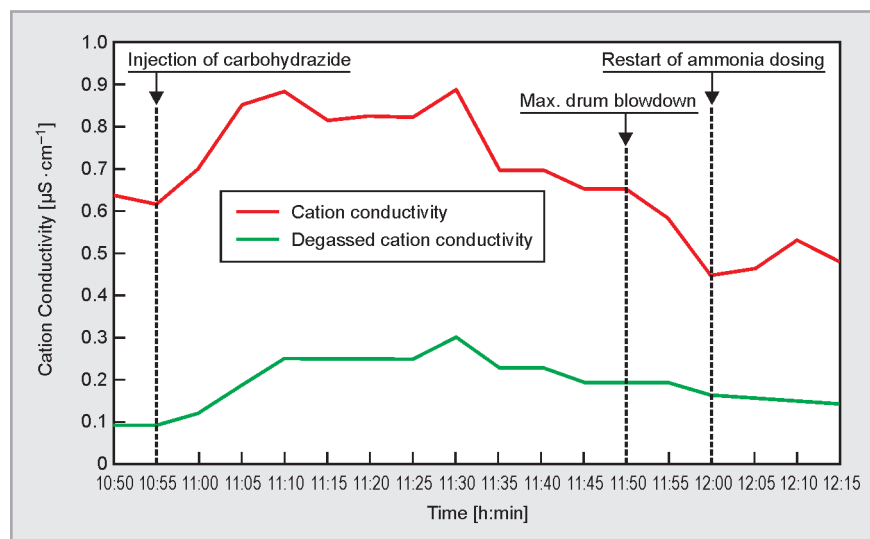


Figure 9: Commissioning data of a combined cycle power plant (a triple-pressure HRSG: 5 bar, 30 bar, and 125 bar steam pressure; air-cooled condenser).

The major task was to measure the cation conductivity of the high-pressure steam before it is sent to the steam turbine. The cycle was treated with ammonia and – exclusively during startup – with carbohydrazide. The gas turbine was started at 08:30 (courtesy of M. De Wispelaere).

Peter Wuhmann (Ph.D., Analytical Chemistry, Swiss Federal Institute of Technology (ETHZ), Zurich, Switzerland) conducted several years of research work with ion sensitive microelectrodes for intracellular ion measurements at the Institute of Cell Biology at the Swiss Federal Institute of Technology (ETHZ). He was a member of the founding group of Swan Analytical Instruments, where has been responsible for R&D since 1991.

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