MEASUREMENT OF SODIUM IN WATER/STEAM CIRCUITS

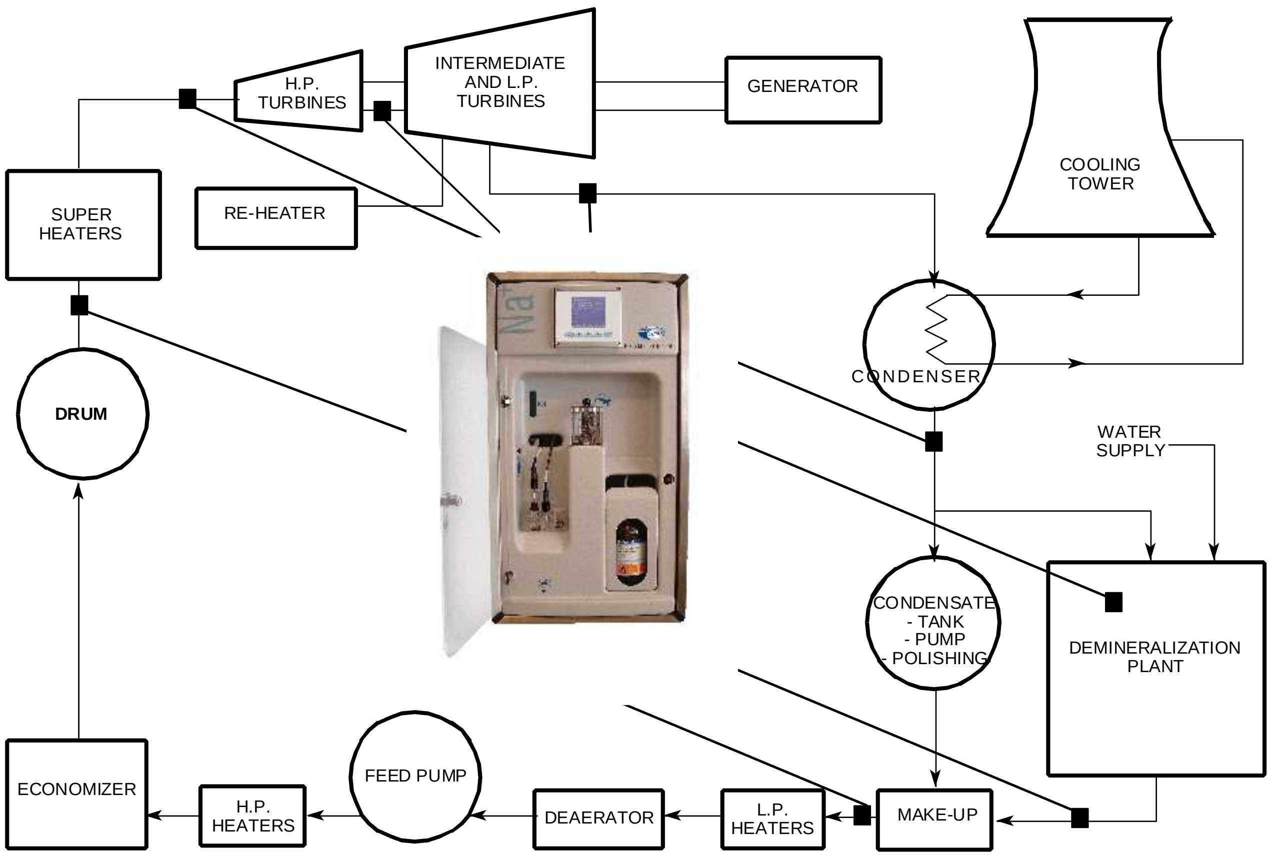

Figure 1: Points of measurement of sodium in power plants water / steam cycle

Water quality is critical to the efficiency and performance of a steam generation plant and to the longevity of its associated equipment. Today, sodium concentration has become one of the most important indexes for water quality throughout the steam and water cycle in power plants. This note discusses the potential risks of poor control and the benefits of measuring sodium with on-line analyzers.

1. Steam

Measurement of sodium in steam before the superheater is strongly indicative of possible stress corrosion in the superheater.

Under the high pressure and temperature conditions of today's power plant, the problem of steam solubility of inorganic compounds is increasingly important. Of particular significance is the steam solubility (in addition to carry-over) of sodium salts, e.g. sodium chloride (NaCl) and sodium hydroxide (NaOH), because of the possibility of stress corrosion cracking in the superheating section.

The measurement of sodium directly in steam immediately before entering the superheater is now recognized as being strongly indicative of possible stress corrosion in the superheater.

It should be noted that corrosion will occur only if sodium is present together with chlorides or hydroxide anions and not, for instance, with sulfates. Chlorides and hydroxides are corrosive, not the sodium, which serves only as the carrier.

Specifically for plants with low boiler pressure (40-80 bars), since non-volatile boiler treatments are typically sodium based (i.e. a mixture of sodium phosphate tribasic and sodium phosphate di-basic), the measurement of sodium in the steam is an excellent indication of mechanical carryover from the drum into the steam.

2. Condensate

Sodium measurement should be the preferred option for early warnings of excursions on condensates to minimize associated risks.

Condensate polishing plays a vital role in power plant cycle chemistry, providing the means to reduce the transport of metal oxide and ionic impurities to the steam generator during all modes of operation, particularly during start-up and upset conditions. The benefits of condensate polishing are:

- Reduced delays to commissioning and start-up as a result of chemistry transients
- Protection of the steam generator during impurity ingress such as with condenser in-leakage
- Reduced impurities fed to steam generators, thereby minimizing the frequency of chemical cleaning
- Improved steam purity resulting in less turbine deposition and phase transition zone corrosion
- Virtual elimination of chemically influenced boiler tube failures
- Attainment of the high degree of feedwater purity necessary for chemical programs such as oxygenated treatment for drum and once-through boilers

Careful management of condensate polishing systems is essential; otherwise polishing plants can become a source of ongoing feed system pollution. Extracting the maximum benefit from condensate polishing systems continues to be a top priority among many electric utility plants.

Although cation and specific conductivity are used frequently to detect excursions in the water/steam loop, it is no longer sufficiently sensitive to measure the very small condenser leaks which have assumed greater importance in modern plant designs. In everyday conditions, with possible temperature, pressure and flow upset or high conductivity background levels, the minimum meaningful variation will be 0.02 mS/cm . This corresponds to 11ppb sodium.

Sodium analysis is much more sensitive. A Hach 9245 sodium analyzer can accurately measure below 0.1ppb. This is 100 times more sensitive than a conductivity measurement. Just as water quality is critical, early signs of excursions are also critical; sodium measurement should be the preferred option to minimize risk.

Steam purity can be more accurately assessed by measuring sodium concentration in both steam and condensate, thus determining the “sodium balance.” The two concentrations should be equal. A higher level of sodium in the condensate indicates a condenser leakage. A lower level of sodium in the condensate indicates deposition of sodium in the steam circuit (on heat transfer surfaces, on turbine blades, etc.).

Sodium measurement is the only technique that achieves accurate and rapid response at any time to detect hydroxides and chlorides known to be contributory factors in the stress-corrosion of austenitic steel.

The origin of the desuperheating water is the condensate water. The quality of the desuperheating water must be without any doubt. If it is contaminated, this contamination will be brought directly into the desuperheated steam. The section most likely to be affected is that part of the superheater immediately following the point at which the desuperheater spray water is injected. It is made in austenitic steel for its mechanical behavior (low thermal dilatation coefficient), but it is more sensitive to corrosion (increased percentage of iron versus carbon). To avoid the catastrophic effect of impurities in the desuperheating water, any excursion must be detected as quickly as possible.

On-line sodium measurement is the only technique that achieves accurate detection of excursions. A HACH 9245 sodium analyzer will ensure a rapid response at any time through regular reactivation of the electrode.

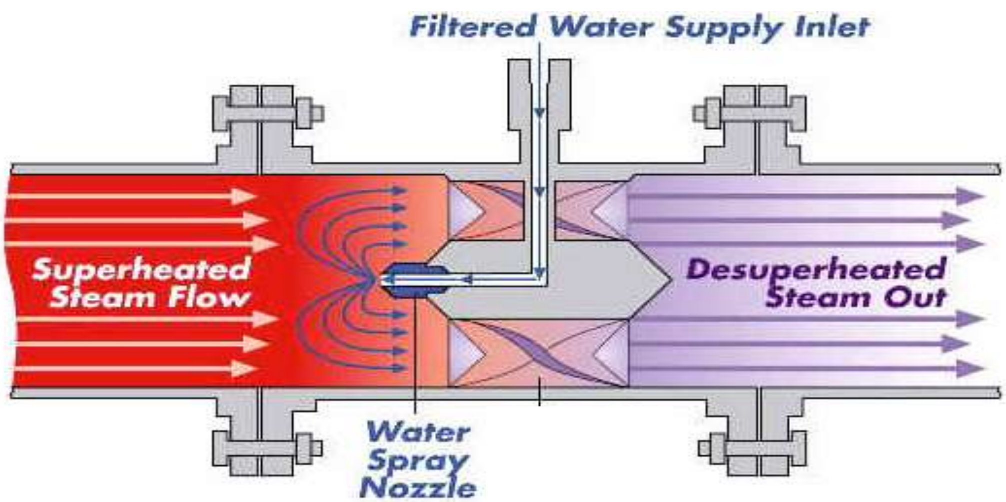

Figure 2: Reverse flow type axial desuperheater

3. Demineralization Plant

For a demineralization plant, on-line sodium measurement is all about ion exchange resin management. Customer benefits are:

- Better utilization of the resin capacity.
- Minimize sodium breakthroughs.
- Optimize acid rinse-out
- Optimization of regeneration cycles.

Cation resin bed exhaustion and its regeneration timing can be monitored with high sensitivity and reliability using on-line sodium analyzers.

Cation resins remove cations such as sodium (Na^+). Sodium is the first cation that breaks through when the cation resin bed is exhausted.

Measuring sodium immediately after cation resins gives an early warning of breakthrough. Removing the saturated resin bed and replacing it with a new (regenerated) one protects the ion exchange capacity of the mixed-bed resins installed farther down the stream.

Quality of the incoming water, the resin quality itself and temperature modifies the ion exchange capacity of the cationic resin bed. This influences the time before the next regeneration. When this time is indicated by a simple volume of sample running through the resin, it is an estimate that may lead to saturation and breakthrough or underuse of resin capacity. On-line measurement of sodium allows regeneration of the cation resin as required.

After mixed bed resin, on-line sodium analysis ensures the quality of the demineralized water delivered to the make-up plant.

Mixed-bed resin contains a mixture of both cation and anion exchange resins for a fine polish of the pure water. It reduces any contaminant left in the pure water.

Remarkable progress has been made over the past decade to reduce the levels of contaminant ions in the treated water from of mixed beds. Specifically in Nuclear plants (PWR), mixed-beds treated water purity is reported in steady state values at 25 to 35 ppt for sodium.

Here, sodium analyzers are used to monitor the final water quality, acting as a final check of quality. HACH 9245 sodium analyzers are used to check the quality of the final water down to 20 ppt levels.

Additionally, a malfunction of the regeneration cycle of the mixed-bed resin is detected by sodium monitoring. Release of sodium can happen by accidental caustic release when there is insufficient rinsing of the mixed-bed anion resin. Again, the warning comes earlier and with higher precision with a sodium analyzer than by conductivity.

4. Range of measurement

Sodium levels lower than 1 ppb are commonly found at the mixed bed output, both in the steam circuit and in the condensate.

Levels of 0 - 10 ppb can be found under normal working conditions at the cation exchangers output, but this can become as high as 100 ppb at the resin exhaustion or in boiler water.

Table: Steam purity requirement *

Steam turbine manufacturer's purity requirement	ABB	GE	Westinghouse
Sodium, ppb (mg/L)	10	20	5

* Data from tech. paper, "CONDENSATE CONSIDERATION"- - DOW Chemical, 1999

Mixed bed outlet	Regular	Nuclear	With latest resin-resin separation technique**
Sodium, ppb (mg/L)	< 0.1	0.015 – 0.035	< 0.01

** Data from ESAA Conference paper, 2005, JD Aspden

4.1. VGB guidelines – Fossil

The VGB guidelines are regularly published by the European Technical Committee combining European Power Plant Supplier's Association (EPPSA), FDBR (organization of professional builders of Steam boilers, vessels and piping), and Technische Vereinigung der Großkraftwerksbetreiber e.V. (VGB). This committee includes representatives from most EU countries.

The difference for sodium in the steam of Fossil power plants is revealed in

Steam for Steam Turbines				
Sodium (Na)	µg/kg		Boiler Water Treatment AVT or Caustic	Boiler Water Treatment Phosphate
		Normal Level	< 2	< 5
		Action Level 1	5	10
		Action Level 2	10	20
		Action Level 3	20	40

Table 1 below:

- Low pressure boilers (under 900 psig - 60bar) will run with phosphate treatment and sodium levels are high (from 5 to 50ppb).
- Higher pressure boilers (>900psig - >60bar) required stricter water/steam quality reflected by lower sodium levels (from 2 to 20ppb)

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		Action Level 2	10	20
		Action Level 3	20	40

Table 1: VGB guidelines: Requirements on steam for condensing turbines[1]

[1] Source: New VGB Guideline for Feed Water, Boiler Water and Steam Quality for Power Plants / Industrial PlantsVGB R 450 Le, by Ulrich Staudt (VGB PowerTech)

4.2 VGB guidelines - Nuclear

These guidelines are based on the primary and secondary side operating chemistry experience gained by VGB members since the beginning of the 1980’s.

VGB recommends these values for secondary side applications (in PWR, Candu, VVER, and AGR secondary cycles).

Steam generator control parameters for power operation:

Control Parameter		Normal Operating Value	Action Level 1	Action Level 2	Action Level 3
Cation conductivity[2]	$mS \cdot cm^{-1}$	< 0.2	> 1.0	> 2.0	> 7.0
Sodium		<0.005	> 0.05	> 0.1	> 0.5

Table 2: VGB guidelines, steam generator on secondary side system[3]

5. Hach 9245 Sodium Analyzer

The Hach 9245 sodium analyzer provides as standard:

- Sample quick-loop at the bottom of the analyzer for an immediate fresh sample
- Minimum sample flow detection and associated alarms
- Vessel for manually-introduced grab sample and fully automatic return to on-line measurement
- pH conditioning using venturi principle with programmable pH set-point
- Temperature compensation based on isothermal point
- Automatic reactivation of sodium electrode by injection of non-hazardous chemical
- All items mounted on a panel

The Hach 9245 Sodium Analyzer is typically used:

- As the enclosure version for all demineralization plants and condensate monitoring. Analyzers may be installed at many points with the attendant risks of dust, water and condensation from day/night temperature differences. In this environment, the enclosure version is preferred.

- As the panel version for Drum, HP or LP steam monitoring. There is usually an "analyzer room" with all sample tubing running to a single panel to easily view several analyzers at the same time or to view grab samples for manual cross-checking. The "room" usually has standard room temperature and low risk of water splashes or leaks. Space is limited on each panel and the panel version is preferred.

[2] Caused only by strong anions; organics or CO2 are not to be considered
[3]Dr. Harry Neder (NPP Isar, Essenbah, Germany) VGB-Primary&Secondary-side-water-chemistry.pdf, May 2007

The fully featured 9245 Sodium Analyzer has an automatic calibration option. This works by multiple injections of known volumes of a concentrated sodium standard solution (10ppm Na^+). This type of solution is easy to prepare and is not sensitive to contamination from the environment or from the container. With only 500mL of calibration solution, the 9245 Sodium Analyzer will run 20 calibrations, which allows the analyzer to run without additional calibration for 5-6 months . The calibration frequency is freely programmable either on number of hours or a fixed date and time. Customer benefits:

- Increased confidence in the analyzer by eliminating all risk of deviation due to human error.
- Increased analyzer up-time with fully automated calibration, including return to on-line analysis.
- Increased availability of analyzer to on-site lab personnel ; increased availability when monitoring a critical on-line process by programming the automatic calibration in fixed date and time mode during the normal regime of the process.

6. The Hach 9240 Sodium (multi)

The Hach 9240 Sodium (multi) Analyzer provides as standard:

- A real, fully-integrated multi-channel analyzer, capable of 1 to 4 channels.
- Auto-adapted rinsing sequence to reach accuracy in minimal cycle time (10 minutes possible). This eliminates carry-over effects and maximizes the number of readings per channel per unit of time.
- Sample "quick-loop" per channel for an immediate fresh sample.
- Minimal sample flow detection and associated alarms.
- Overflow vessel to allow variations in inlet pressures and for manually introduced samples.
- Manually prompted samples are followed by an automatic return to on-line measurement.
- pH conditioning using a siphon effect on a liquid sample column with programmable pH set-point.
- Temperature compensation based on an isothermal point.
- Regulated addition of conditioning solution to the sample across both pH and temperature ranges.
- Automatic reactivation of the sodium electrode by injection of a non-hazardous chemical.

7. Product selection depending on application

The 9245 Sodium is recommended as the solution of choice when several sample points are considered and every time one of the following points is raised as a key application feature:

- Response time must be less than 3 minutes.
- Analyzers are as close as possible to sample points (minimize piping).
- The impact of Electronic or Mechanical failure must be minimal.

There is a strong need to separate channels and to use the 9245 Sodium when:

- Samples have a difference in sodium greater than 200ppb.
- Temperature difference may be greater than 20°C from one channel to the next.
- Any sample where pH is less than 5.

The 9240 Sodium (Multi) is recommended when any of the following points are important:

- The initial cost, the cost of ownership (and spares), and the space occupied by the analyzer must be kept to a minimum.
- The process visualization needs to be simple and a single human-machine interface is desired.
- The solution must be expandable: "In the future, we will expand (adding new sample points)."

8. Product selection matrix

- When an application like mixed-bed, steam, condensate and boiler applications are classified standard (0.01 to 10’000ppb)
- For a high acidity water (pH lower than 5; 50 < [acidity] < 250 mg/L $CaCO_3$), such as water from a cation exchanger outlet, the regular gaseous conditioning is not sufficient to raise the pH above 10.3. In that case, the forced-gas conditioning system (K-kit) is required. Diisopropylamine or ethanolamine or ammonia may be used as the reagent.
- Select the final Part Number of the required product using **Error! Reference source not found.** or **Error! Reference source not found.** below

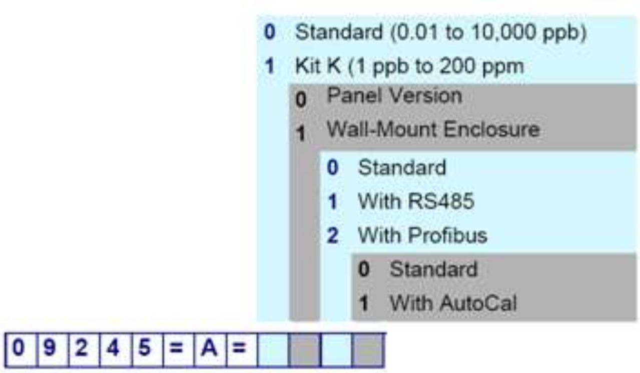

Table 3: identification matrix for model 9245

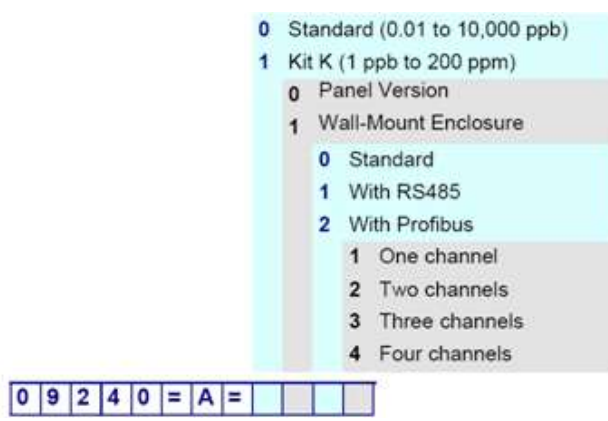

Table 4: identification matrix for model 9245 and 9240

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