



Conductivity After Cation Exchange (CACE), Turbidity & Hydrogen measurement for Cyclic operation

Aditya Kanetkar (Forbes Marshall Pvt. Ltd)

Mar Nogales (SWAN Analytical Instruments AG)



The challenge in cycling plants

- Today's demands require generating units to rapidly respond to **changing generation requirements** and supply fluctuations from renewables such as solar and wind power.
- Many plants worldwide are required to **fast start and to frequently cycle**.
- Given the substantial fuel cost, environmental issues, and economic impact, any **shortening of the time** between start-up and reaching full load is of high importance.

- It is very important to **monitor steam purity**:
 - to demonstrate that it is suitable for admission to the steam turbine with minimal delays to startup times
 - to detect serious cycle contamination during startups

- Conductivity after cation exchanger (CACE) is still the decisive measurement for the start-up of the steam turbine, and the focus is **how fast the CACE** results are below established limit.

Is your SWAS ready for Cyclic Operation?

Feed Water Purity Monitoring during Cyclic operation:

Robust Conductivity After Cation Exchange (CACE) measurement



Corrosion Product monitoring:

Continuous and Quick monitoring of Corrosion products



Corrosion trend monitoring:

Continuous monitoring of corrosion Trends during operation



Robust Conductivity After Cation Exchange (CACE) measurement



Expectation good CACE instrument in Cycling plants

- Frequent start-up and shut-down periods, shorter operation time: important that CACE analyzer should be always **ready to measure**
- **Fast response time and fast stable values** are important
- **Continuous measurement** is necessary to really monitor what happens during all transients
- **Analyzer must starts automatically as soon as sample is available, and stops also automatically if there is no sample**
- During short shut-down periods, sample is still available to analyzers if inlet valves are not closed: faster consumption for traditional cation resin columns

AMI CACE : Features and self-diagnostics capabilities

- Cation resin regenerated and pre-rinsed
- Sample must remain in active resin for ~24s
- Flow from top to bottom
- Automatic air venting
- Diameter / height
- Airtight connections
- Maintenance interval: **EDI technology, cation resin not spent anymore**
- Ease of maintenance



AMI CACE: Features and self-diagnostics capabilities

AMI CACE

Main process value

- Specific conductivity (SC)
- Conductivity after cation exchanger (CACE)
- Calculated pH
- Calculated concentration alkalization agent (ammonia, morpholine or ethanolamines).

Diagnosis values

- Sample flow
- Sample temperature (automatic compensation to reference 25°C)
- EDI current in mA
- EDI voltage in mV

Design features

- Automatic compensation to reference 25°C for SC measurement (i.e., ammonia, morpholine, ethanolamine, others)
- Automatic temperature compensation to reference 25°C for CACE measurement (nonlinear for strong acids)
- Adequate and high precision cell constants for ultrapure water
- Continuous deaeration of EDI module
- Automatic EDI module shutdown if no sample flow, with automatic start-up once sample flow is recovered

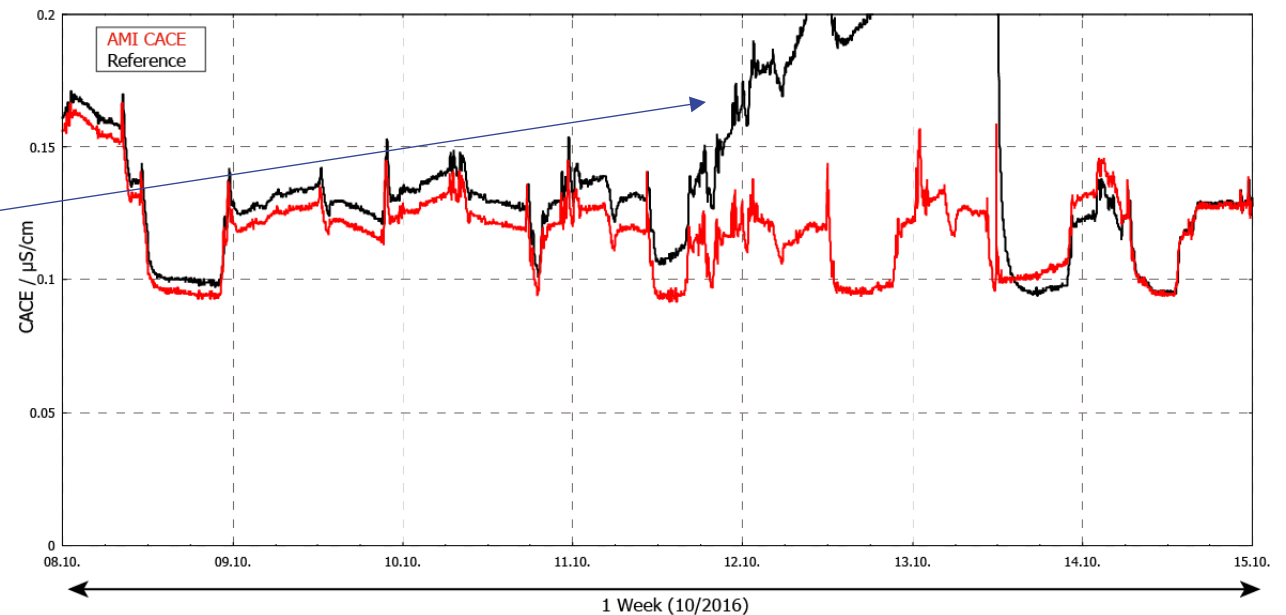
Operational advantages AMI CACE versus traditional cation resin columns

➤ Continuous measurement of CACE

- No downtime by resin exhaustion
- No downtime by new resin pre-rinse time (if continuous resin pre-rinse not available in analyzer)
- Consistent measurements: gaps in valid readings not attributed anymore to exhausted resin column

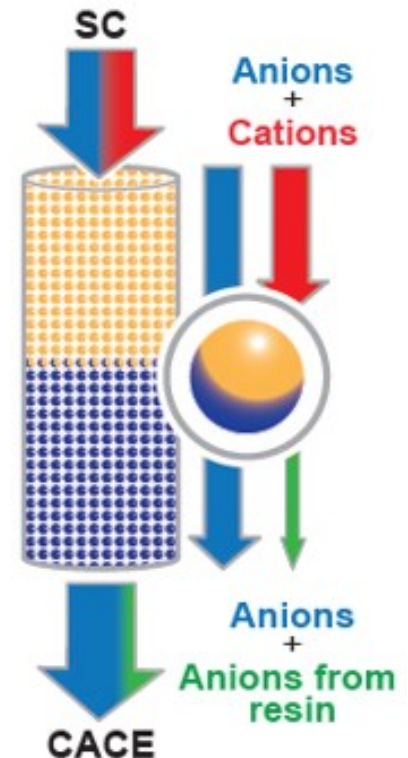
Necessary resin exchange on the reference measurement.

SWAN AMI CACE analyzer
SWAN AMI Deltacon analyzer with pre-rinse option (Reference measurement)



Operational advantages AMI CACE versus traditional cation resin columns

- **Reliable CACE measurement**
- **Reproducible CACE measurement conditions**
 - Resin leakage influences baseline CACE
 - Less anion leaching from resin (due to poor resin quality, resin manufacturing, contact time between resin and sample, ...)
 - No measurement bias caused by resin regeneration leachable products
 - No measurement bias caused by improper regeneration (bad resin exchange capacity)
- **Less sample flow necessary (3 - 4 l/h)**
 - Reduced demineralized water consumption by analyzers
- **Faster stable values after start-up**
 - Smaller resin volume, shorter rinse time to replace old sample

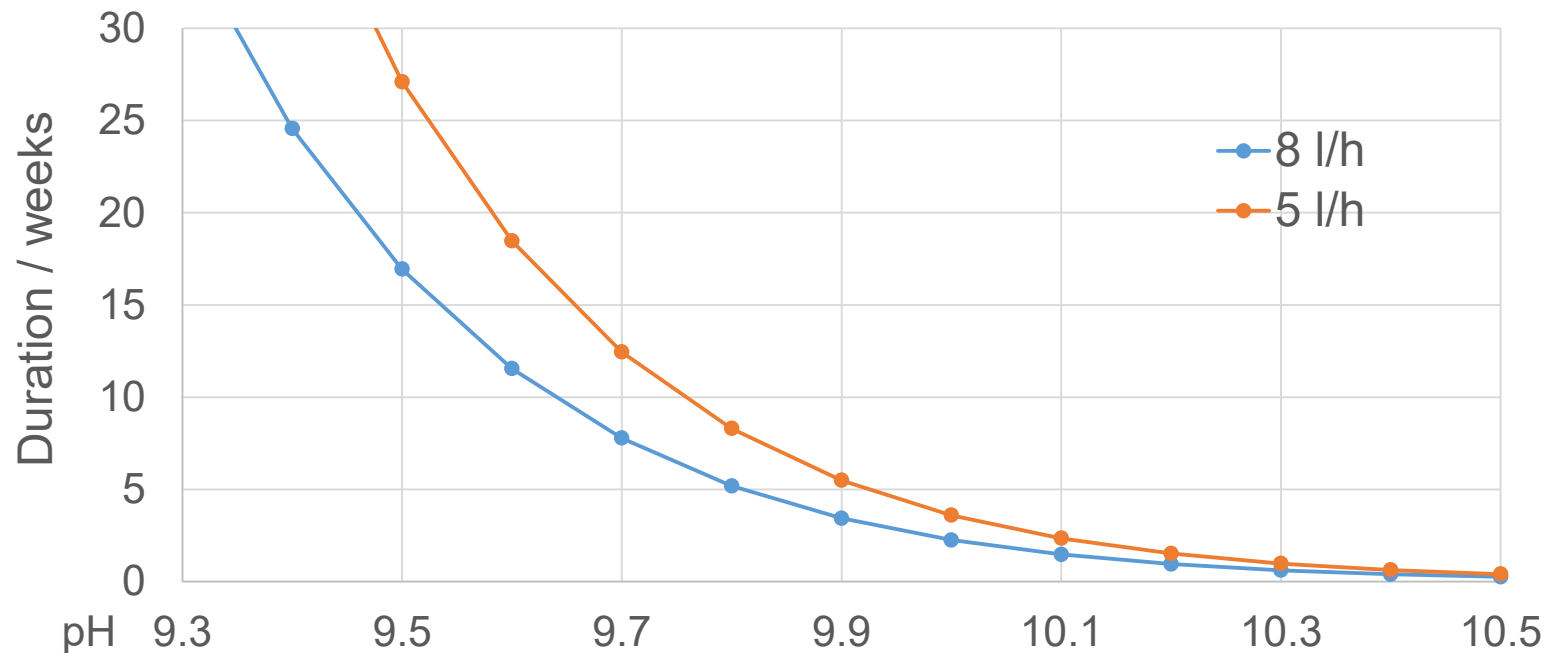


Maintenance advantages

Cation resin consumption

➤ Frequency of cation resin replacement

- It depends mainly on sample flow rate and pH
- Fast resin depletion if sample has high pH



Maintenance advantages AMI CACE versus traditional cation resin columns

➤ **No resin exchange necessary**

- As cation resin is not consumed: continuous and automatic regeneration
- No waste resin

➤ **No resin regeneration necessary**

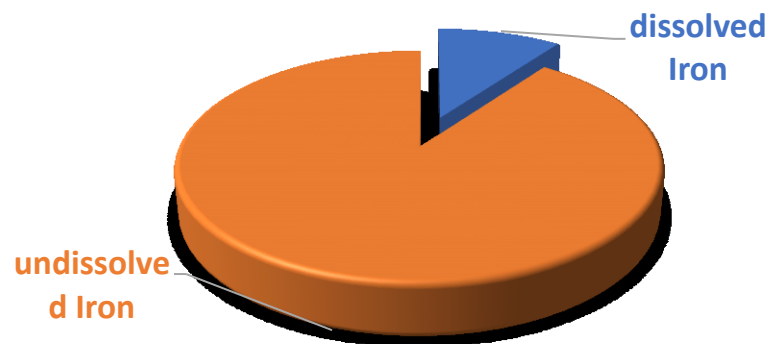
- As cation resin is not consumed: continuous and automatic regeneration
- No hydrochloric acid handling for resin regeneration
- No consumption of demineralized water to wash out the acid and reduce resin leaching (some customers indicated that needed half day rinsing period with demineralized water until water SC is $< 0.2 \mu\text{S}/\text{cm}$ or lower..)
- Reduced man-hours for maintenance activities

Turbidity Measurement for Corrosion Product monitoring



Corrosion products monitoring

- Corrosion product monitoring (e.g., total iron) is essential to determine the effectiveness of applied cycle chemistry treatment program in a power plant.
- The monitoring of corrosion products is required by various standards including IAPWS, EPRI and VGB standards.
- The corrosion products consist of both dissolved and particulate oxides (iron and copper), which are transported and deposited throughout the water-steam cycle.
- The majority – more than 95% – are present as **undissolved particles**:
 - Mixed oxides
 - Various particle sized (mostly < 2 microns or smaller!))



Corrosion products measurement points & Method

Table 2: Summary of key corrosion product sampling locations

Type of Plant	Sampling Locations									
	ACC Outlet*	Condensate Filter Outlet*	Condensate Pump Discharge	Process Condensate Return	LP & HP Heater Drains	Dearator Inlet	Economizer Inlet	Boiler /Evaporator	Saturated or Superheated Steam	
Fossil – All Ferrous	X	X	X		X		X		N/A	
Fossil – Mixed Metallurgy	X	X	X		X	X	X		N/A	
Combined Cycle/HRSG Plants	X	X	X				X	X	N/A	
Cogeneration Plants	X	X	X	X			X	X	N/A	

* If ACC or condensate filters installed

- In flexible power plants, steam is also controlled because cycling may enhance the exfoliation of oxide layers, which may have an impact on the steam turbine and other critical components. [2]



IAPWS TGD6-13(2014)

The International Association for the Properties of Water and Steam

London, United Kingdom
September 2013

Technical Guidance Document:

Corrosion Product Sampling and Analysis for Fossil and Combined Cycle Plants

© 2013 International Association for the Properties of Water and Steam
Publication in whole or in part is allowed in all countries provided that attribution is given to the International Association for the Properties of Water and Steam

President:
Professor Tamara Petrova
Moscow Power Engineering Institute
Moscow, Russia

Executive Secretary:
Dr. R. B. Dooley
Structural Integrity Associates
Southport, Merseyside, UK
Email: rdooley@structint.com

This document contains 39 pages, including this cover page.

This technical guidance document has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in London, UK, 1–6 September 2013, for issue by its Secretariat. The members of IAPWS are: Britain and Ireland, Canada, the Czech Republic, Germany, Japan, Russia, Scandinavia (Denmark, Finland, Norway and Sweden), and the United States of America, and Associate Members Argentina and Brazil, Australia, France, Greece, Italy, New Zealand and Switzerland. The document represents the accumulated experience of the IAPWS Power Cycle Chemistry (PCC) Working Group with representation from 21 countries.

Minor editorial revisions (corrections in References section) were made in 2014.

This technical guidance document considers the sampling and monitoring of total iron and copper corrosion products in fossil and combined cycle HRSG plants.

Further information about this technical guidance document and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS or from <http://www.iapws.org>.

Challenges to Monitor corrosion products online:

- **Total iron** analysis method (with acid digestion of undissolved particles [1]) is only possible in the laboratory:
 - **It is a complex and time-consuming analysis**
 - **Process is too complex for automation (online analysis)**
- Demand for **additional** trend monitor method:
 - Real-time results

The extra challenge during Cyclic Operation:

- Many plants worldwide operate in a flexible manner with frequent startups, shutdowns, and load changes, with higher risk of transportation and deposition of corrosion particles.
- The challenge is to monitor corrosion products during these fast-changing conditions in the plant. By taking only grab samples, the likelihood of missing important events as peaks of mobilized corrosion particles is high

Corrosion product during Quick Startup !!

During start-up...

- ... iron levels exceed values in guidelines
- ... iron levels change rapidly
- ... undissolved particles are mobilized rapidly in the water-steam cycle
- ... representative grab sampling and analysis is not feasible: too frequent sampling required in short time period

As consequence, iron levels are unknown during start-up!



Why is monitored Turbidity?

- The online turbidity measurement **allows continuous monitoring** of the presence and the spiking behavior of corrosion particles during the plant startup, load transient and shutdown.
- Turbidity measurement **helps to evaluate when and where are corrosion products released and transported.**
- It allows also trend monitoring for corrosion particle levels.



Advantage of Turbidity monitoring:

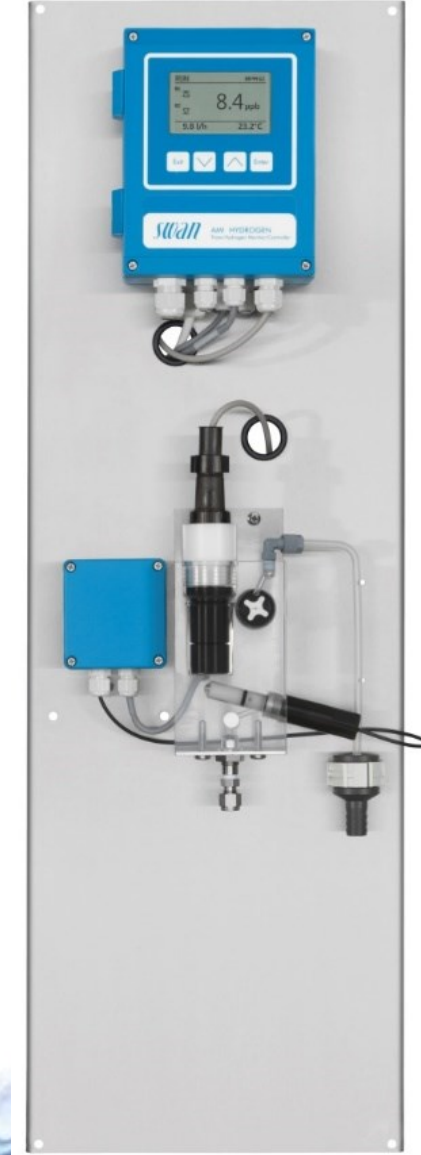
- Turbidity measurement shows very **good sensitivity and high response** to variations in plant load.
- During data evaluation, it is important not only to consider **peaks in turbidity but also the duration of the event** until the turbidity value is stabilized.
- The **correlation of turbidity with the concentration of corrosion products** depends on particle size and distribution, which are individual properties for each plant and can change over time. Therefore, the analysis of total corrosion products in the laboratory is also necessary, with a frequency dictated by the plant operation conditions [1].
- The turbidity analyzer should be equipped with an **infrared light source (860 nm)**, suitable to detect black colored particles (magnetite) and red colored particles (hematite) [2].
- Analyzers with **continuous sample flow monitoring** are important to validate turbidity measurements and disregard turbidity peaks caused by reasons not related to process (e.g., manual intervention by operator).

Monitor AMI Turbiwell Power



- Infrared light source (860 nm)
- **Sample flow meter** with alarm for turbidity measurement validation
- Integrated constant head guarantees a **constant sample flow** into the measuring chamber
- Non-contact turbidimeter: system optics are not in direct contact with sample, no fouling on optical surfaces
- Manual or automated draining of the sample chamber for cleaning
- Due to the non-contact design, **no instrument drift is observed**: calibration free
- Long life LED light source

Dissolved Hydrogen (H₂) Measurement for Corrosion Trends



Why is measured Dissolved Hydrogen?

- The concentration of hydrogen in water can be used as measure of the reaction between the water/steam and the surface of the steel:



Schikorr reaction

- The presence of dissolved hydrogen indicates an active corrosion process.
- Dissolved hydrogen measurement can be used as a **corrosion trend indicator** in certain locations of the water-steam cycle, to take the necessary action to mitigate corrosion.

Sources of H₂ in the water-steam cycle

Growing of protecting layers on steel surfaces

- If steel and water or steam get in contact, the first step of the formation of an oxide layer is the oxidation of Fe to Fe(OH)₂:



- Under the boundary conditions in the water-steam cycle, especially at temperatures >200°C, Fe(OH)₂ will be further oxidised as per **Schikorr**:



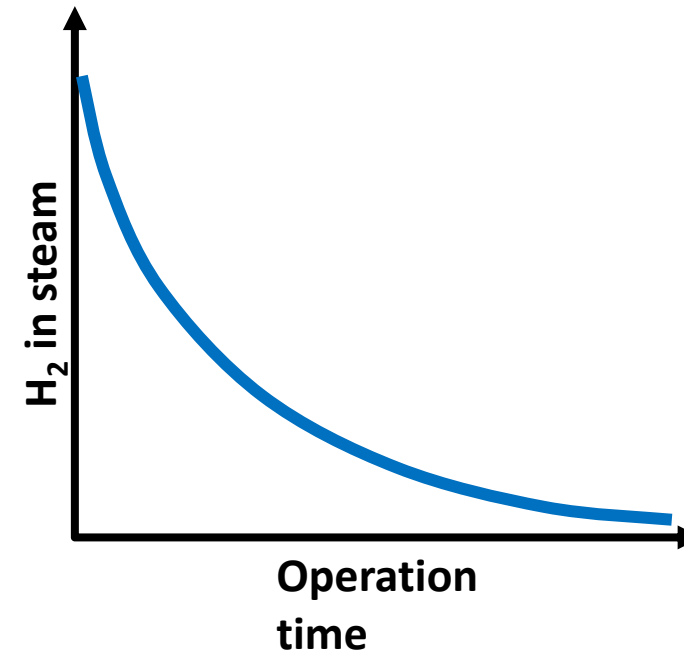
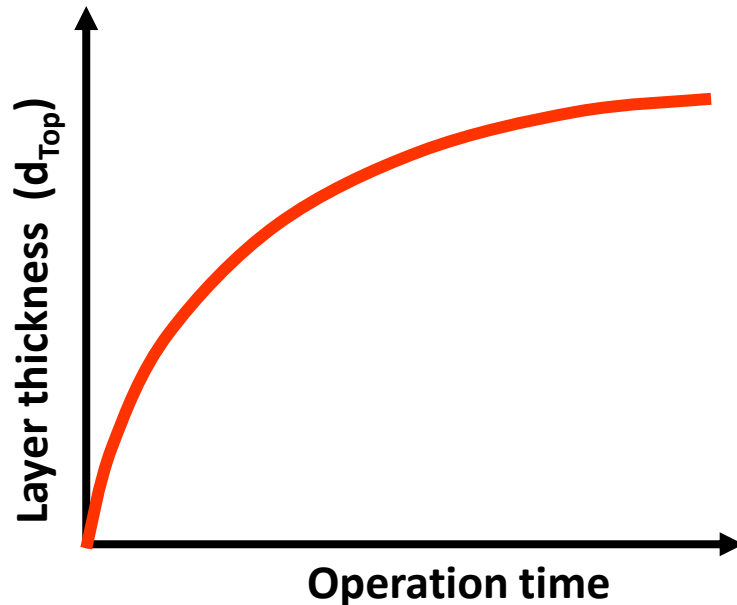
- At temperatures > 300°C a spontaneous oxidation takes place as:



Sources of H₂ in the water-steam cycle

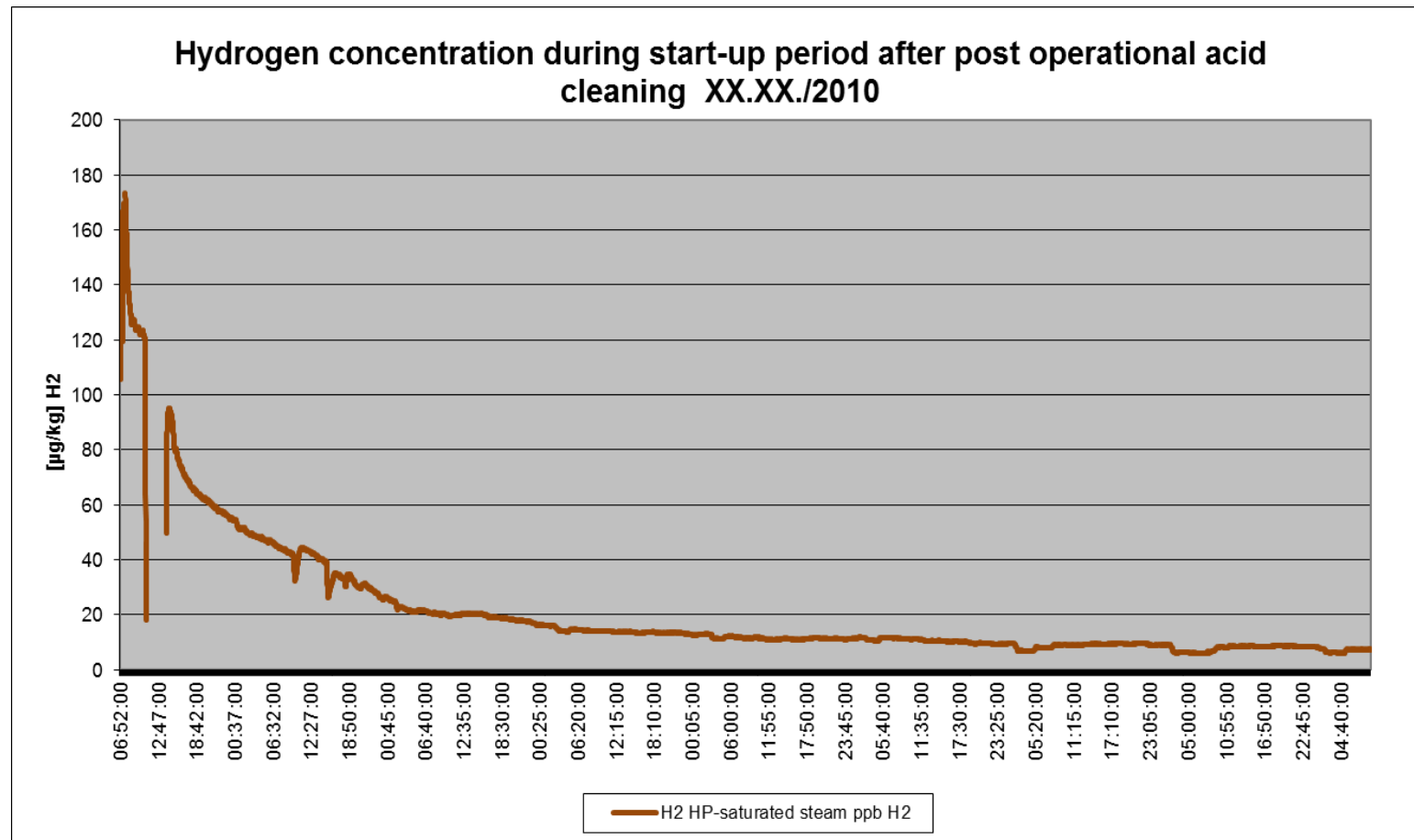
Growing of protecting layers on steel surfaces

- With increasing thickness of the magnetite layer on the material surface, the diffusion of iron and oxygen becomes more and more hampered: due to this, the H₂-concentration decreases in dependence to the operating time.
- If the quality of the **feed water is adequate** and the **formation process of magnetite is undisturbed**, after about 5000 hours of continuous operation a H₂-concentration of $\leq 2\mu\text{g}/\text{kg}$ can be expected in the steam.



Sources of H₂ in the water-steam cycle Growing of protecting layers on steel surfaces

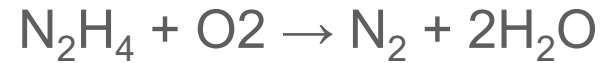
Hydrogen concentration during start-up period after post operational acid cleaning



Sources of H₂ in the water-steam cycle

Application of hydrazine treatment for conditioning

- The reaction of hydrazine with residual oxygen is:



- Besides to this, there are several competitive decomposition reactions taking place in parallel. One decomposition product of some of these reactions is hydrogen:



or:



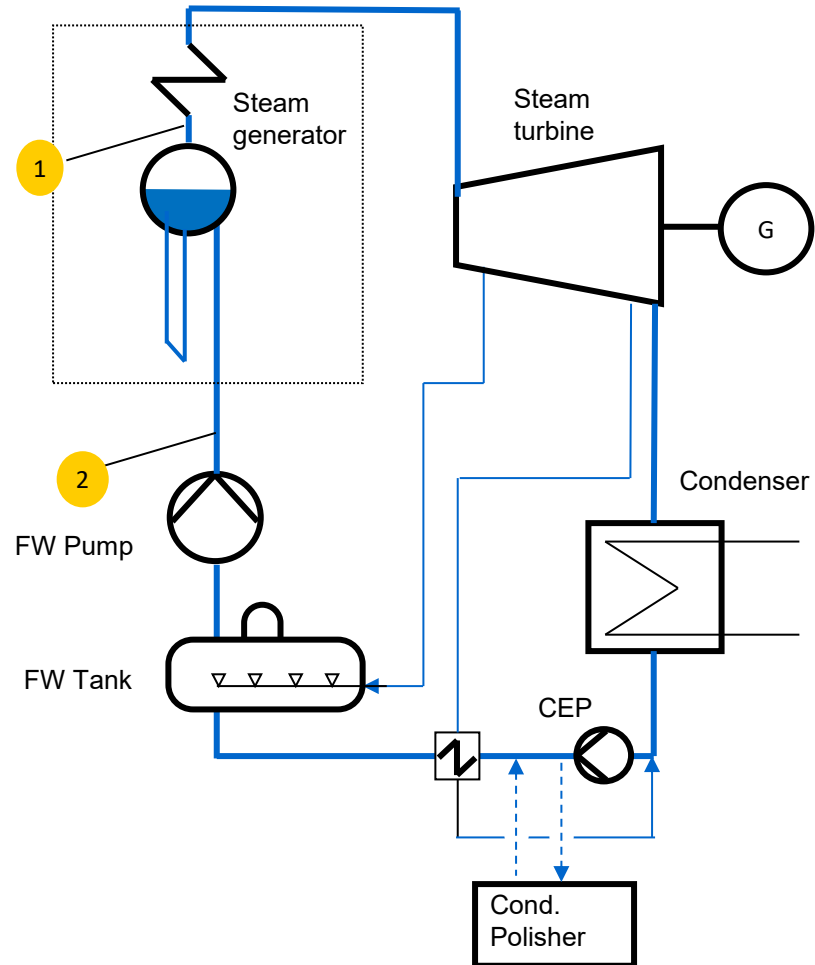
Sources of H₂ in the water-steam cycle

Application of organic chemicals for conditioning

- If organic chemicals like amines are applied, these substances generally suffer from thermal decomposition.
This may also be associated with the release of hydrogen. The extent of the release of H₂ is affected by:
 - the kind of chemical substance and its thermal stability
 - operating parameters of the steam generating system, especially the medium temperature

- Due to the vast variety of options, a reliable assessment of the influence of the thermal decomposition to the hydrogen concentration is not possible.

Dissolved hydrogen measurement points



Typical monitoring points

- 1 **Saturated steam** (if H₂ is generated due to ongoing corrosion processes in the drum, H₂ will be present mainly in the saturated steam phase)
- 2 **Feedwater – Economizer inlet** (vent at deaerator should be closed to have a representative H₂ measurement)

H₂ concentration reference values

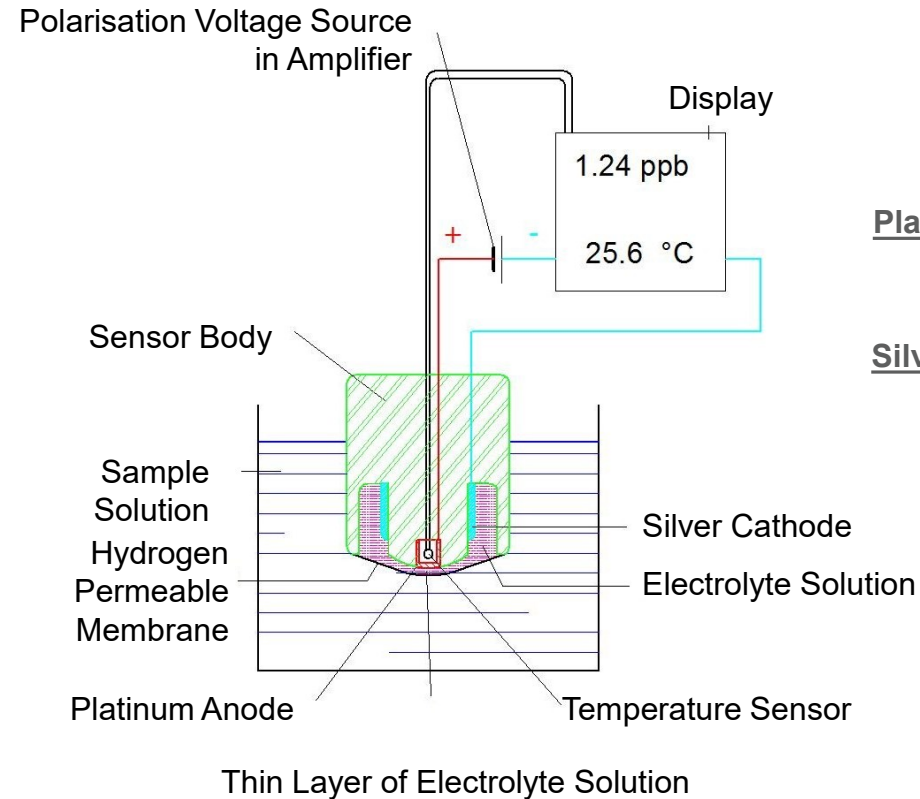
- The normal dissolved hydrogen level can change from plant to plant: **continuous monitoring is used at each individual plant to determine a baseline level.**
- Guidelines for chemistry in Power plants do not indicate maximum H₂ values: each plant must establish their baseline concentration, to detect ongoing corrosion processes if the H₂ concentration increases.
- For the interpretation of H₂ readings in the water-steam cycle, it is indispensable to measure as well other quality parameter (like pH-value or SC, O₂ and CACE) and process parameters (mass flow, load, etc..).

Measurement principle Aerometry

- Small polarization is applied between two electrodes.
- Hydrogen is oxidized at the anode (platinum electrode):
$$\text{H}_2 \rightarrow 2 \text{H}^+ + 2\text{e}^-$$
- At cathode (silver-silver chloride electrode), silver chloride is reduced to element silver:
$$\text{AgCl} + 2\text{e}^- \rightarrow \text{Ag} + 2\text{Cl}^-$$
- If more electrons get transported, then it will increase the electrical current. This current is directly proportional to the concentration of hydrogen in the sample.

Measurement principle

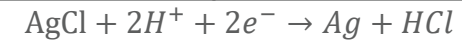
Clark-type hydrogen sensors



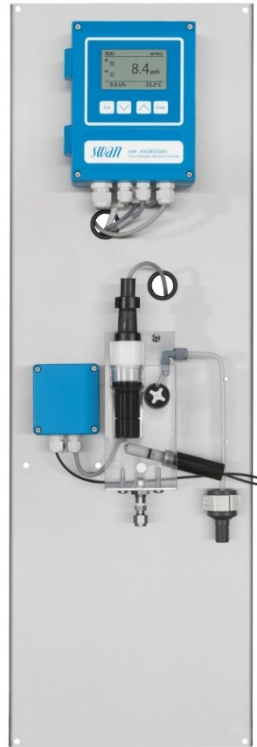
Platinum Anode (Working Electrode)



Silver Cathode (Counter Electrode)



SWAN Hydrogen analyzers



AMI Hydrogen QED Monitor



AMI Inspector Hydrogen

Monitor AMI Hydrogen QED



- Monitor for continuous measurement of dissolved hydrogen in water
- Measurement range: 0.01ppb to 800ppb of dissolved hydrogen
- Accuracy $\pm 5\%$ of the reading, or ± 0.5 ppb
- Automatic sensor verification and self diagnosis with **integrated Faraday verification system**
- Integrated NT5K temperature sensor
- Sample flow surveillance and needle valve for sample flow regulation.

Monitor AMI Hydrogen QED Faraday verification

- The Faraday verification is used to check the sensor periodically, with intervals that can be freely programmed.
- Known amount of **hydrogen gas** will be produced for the given **electricity (current)** in the system.



Faraday Second Law:

$$n = \left(\frac{It}{F} \right) \left(\frac{1}{z} \right) \Rightarrow n \propto I$$

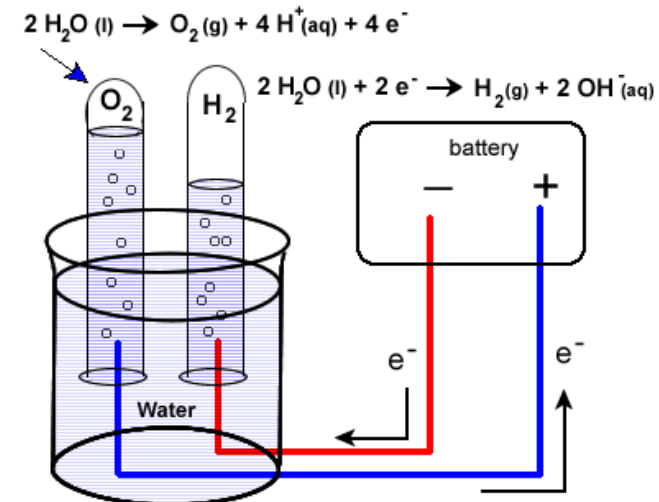
n is the amount of substance

I is current passed through the substance

t is the total time the constant current was applied

$F = 96485 \text{ C mol}^{-1}$ is the Faraday constant

z is the valency number of ions of the substance (=1 for hydrogen).



Conclusions

- ✓ Dissolved hydrogen is an ideal parameter for the assessment of the formation of protecting layers (magnetite) and the interaction between water and steel.
|
- ✓ The normal dissolved hydrogen level can change from plant to plant: continuous monitoring is used at each individual plant to determine a baseline level.
- ✓ For the interpretation of dissolved hydrogen readings in the water-steam cycle, it is indispensable to measure as well other quality parameters (like pH-value or SC, O₂ and CACE) and process parameters (mass flow, load, etc..).
|

THANK YOU FOR YOUR ATTENTION ANY QUESTIONS?

