GREEN HYDROGEN INDUSTRY

Solutions for Monitoring Water in Green Hydrogen Production

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Save money, extend equipment life and optimize electrolyzer efficiency with continuous water quality monitoring

Reliable, high quality water is critical to hydrogen production. The booming pipeline of global clean hydrogen projects will demand over 2 million m^3/day (528 million US gallons/day) of demineralized water for electrolysis processes by 2030.

At a molecular level hydrogen production demands 9 kg or liters of high-quality demineralized water per 1 kg of hydrogen produced. However, over time trace level residual water impurities not adequately removed in pretreatment processes such as demineralization or reverse osmosis can carry over and accumulate inside Alkaline and Proton Exchange Membrane (PEM) electrolysis cells critical to hydrogen production. Additionally, impurities are generated inside the electrolyzer process itself.

What are the impacts and risks of accumulating residual impurities in hydrogen electrolysis cells?

Cumulative results of water impurity carryover include:

- Shortened maintenance interval and costly component replacement
- Increased electricity consumption per output and reduced efficiency
- Increased Levelized Cost of Hydrogen (LCOH)

Poor water quality is a primary cause of clogging and deactivation of membranes, leading to stack failure in PEM electrolysis and reduced lifetime of electrolyzers.

Limitations of electrical conductivity (EC)

As a common indicator of ionic contamination, EC is an important water quality parameter but cannot be the only one used to continuous monitor pure water for hydrogen electrolysis. This is because EC in high purifity water is sharply affected by atmospheric contact, permitting dissolution of small amounts of CO_2

As water approaches absolute purity, its conductivity approaches that of pure water, 0.055 µS/cm. An EC of 0.058 µS/cm may indicate extra sodium or CO_2, but the difference in EC is almost unmeasurable. EC is non-specific and cannot predict contamination source (i.e. if it comes from acid, base or salts). In highly pure water [refence Table 1] other parameters, including dedicated equipment for turbidity, sodium, chloride, silica and organic carbon are monitored to determine contamination source.

Parameter	Water Quality Type I	Water Quality Type II
Electrical conductivity at 25°	0.0555 µS/cm	< 1.0 µS/cm
Electrical resistivity at 25°C.	>18 MΩ·cm	>1.0 MΩ·cm
Total organic carbon	< 50 µgC/L	< 50 µgC/L
Sodium	< 1 µg/L	< 5 µg/L
Chloride	< 1 µg/L	< 5 µg/L
Total Silica	< 3 µg/L	< 3 µg/L
Heterotrophic bacteria count	< 10/1000 cfu/mL	< 10/1000 cfu/mL
Endotoxin	< 0.03/0.25 EU/mL	< 0.03/0.25 EU/mL

Table 1: ASTM D1193-06 (Standard Specification for Reagent Water)

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Green Hydrogen Production Electrolyzer Process Diagrams

Green hydrogen production processes include source water treatment, process water treatment and electrolyzer systems. The most common types of electrolyzer systems are alkaline and Proton Exchange Membrane (PEM).

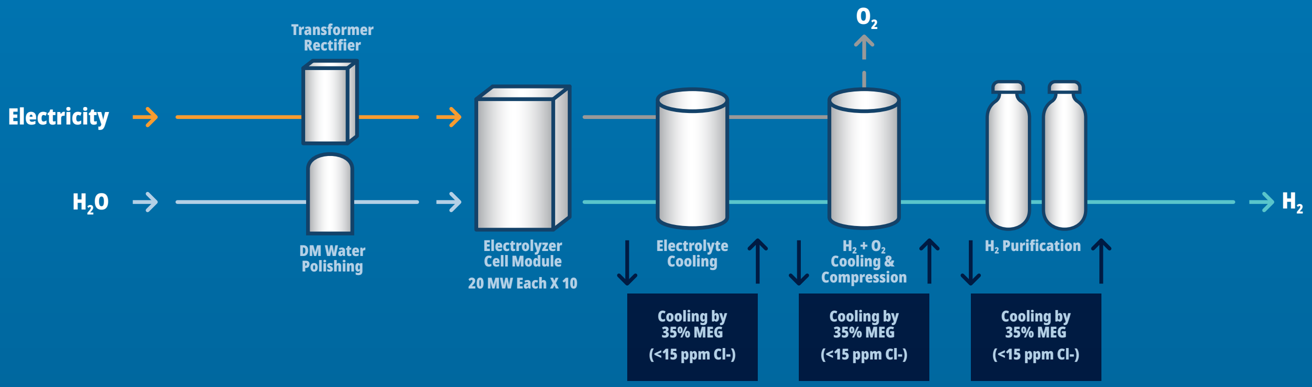

Diagram 1: Electrolyzer (200MW PEM)

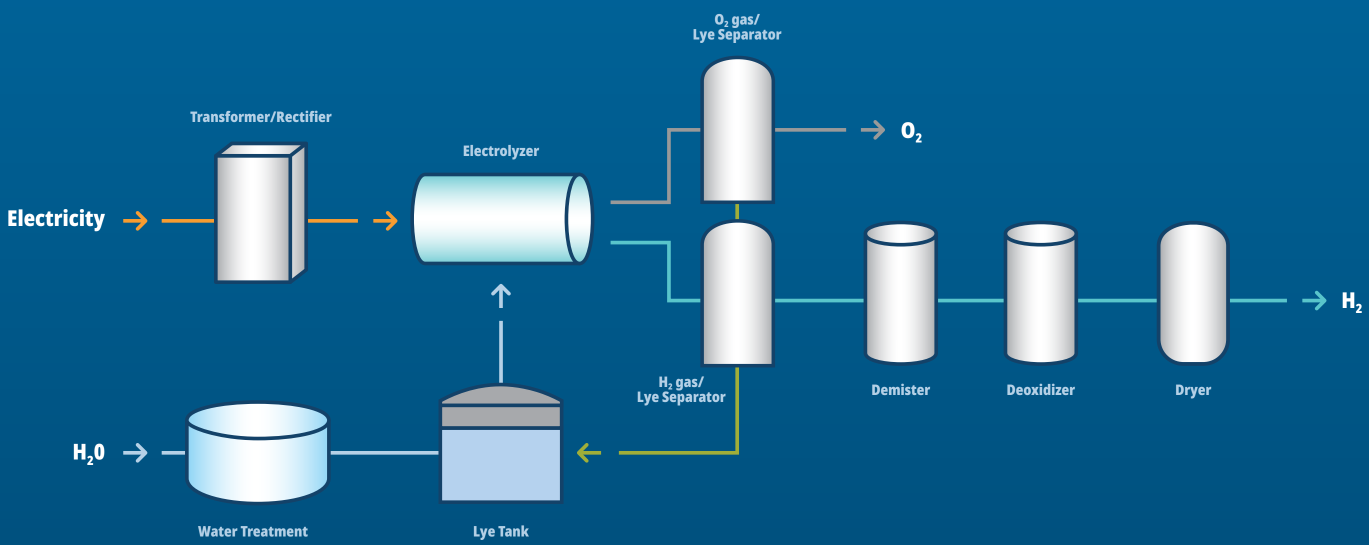

Diagram 2: Alkaline Electrolyzer

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Green Hydrogen Production Water Pretreatment Diagrams - Where Parameter Monitoring is Needed

Required water pretreatment varies depending on the supply source and electrolyzer feedstock specifications. In the block diagrams below unit processes are in light blue; water quality parameters are in green.

Water Quality Parameters

pH	pH
R/O	REDOX/ORP
TOC	Total Organic Carbon
S	Silica
C	Conductivity
T	Turbidity
DS	Dissolved Silica

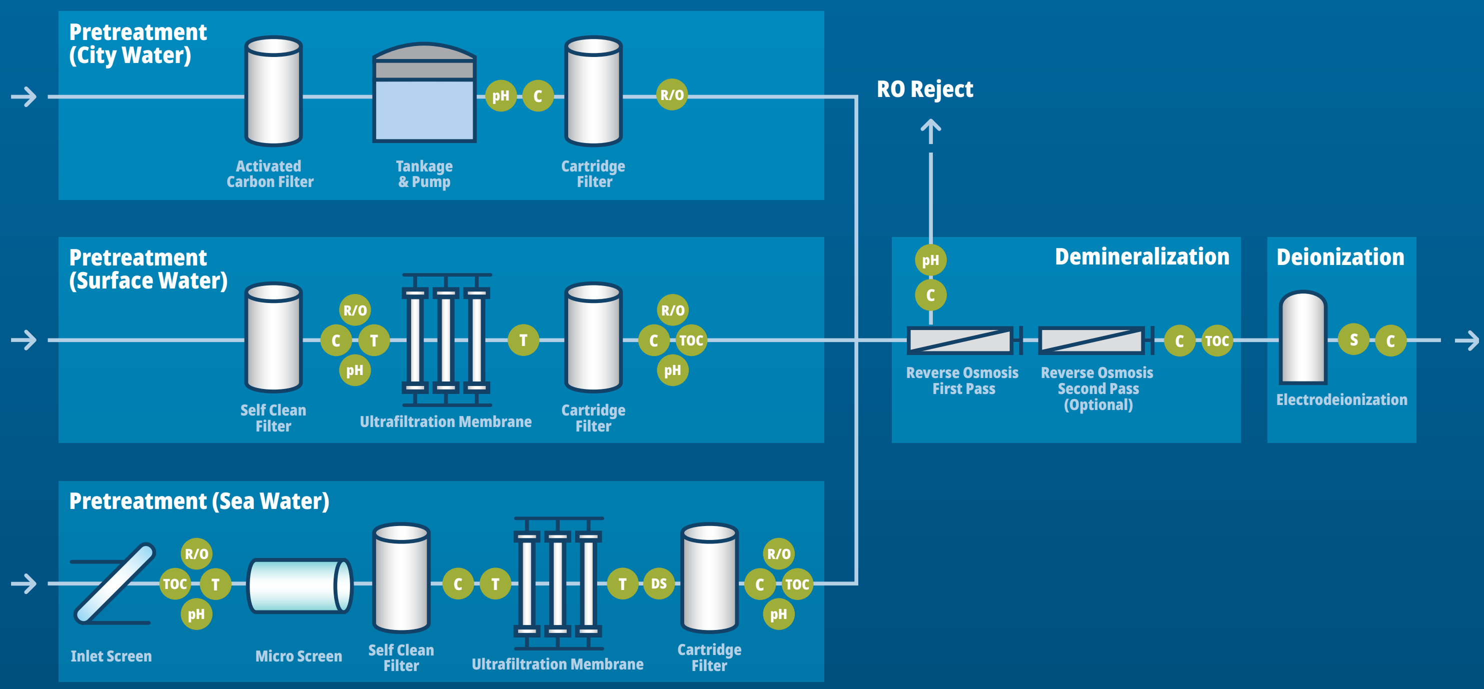

Diagram 3: Typical Block Flow Diagram – Water Preparation

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Impact of water quality in hydrogen production

Key Parameters

Specific or Direct Conductivity: Conductivity is measured at several points of the pure water preparation process, typically with in-line, temperature compensated conductivity sensors. In PEM electrolysis cells conductivity is measured in continuous polishing loop. While economic to measure at several points, electrical conductivity is non-specific and cannot predict contamination source (i.e. if it comes from acid, base or salts).

pH: In pure demineralized water (conductivity of 0.06 µS/cm), the pH must be between 6.9 (traces of strong acid-HCl) and 7.2 (traces of strong base-NaOH). Very high or low pH indicates that scale is forming on Reverse Osmosis (RO) membranes used in water demineralization. Monitoring in the water demineralization stage allows operators to make trim acid/base adjustments that prevent RO membrane fouling and in turn minimize hydrogen production disruptions (for offline cleaning and replacement).

Redox / Oxidation Reduction Potential (ORP): In water preparation oxidants are widely used for disinfection however concentration must also be maintained at very low levels prior to reserve osmosis (RO) membrane to prevent deterioration. While ORP is a well-established measurement principle, it is less specific than ultra-low range chlorine measurement and not ideal as a control parameter for membrane protection in reverse osmosis systems. While ORP provides a fast response to presence of oxidants (such as chlorine) in water, it is an indirect, non-specific parameter with a matrix of influences (sample pH, flow/pressure, etc.), resulting in a slow non-linear response to dechlorination. Correlating ORP surrogate measurement values to RO membrane risk may result in overfeeding dechlorination agents such as sodium bisulfite.

Sodium: Indicates breakthrough (from demineralization) which can lead to stress and pitting of corrosion resistant alloys in electrolyzer cell modules. Managing salt as a solid has high capital and operating costs. Salt valorization (mineral recovery) is in active consideration in some projects.

Silica: Indicates anion breakthrough (from demineralization). In PEM systems the higher pressures contribute to formation of silica film on water polishing RO membrane surfaces and on exchange membrane solid polymer electrolyte. Silica deposits insulate the exchange membrane, resulting in higher electricity usage to produce the same quantity of hydrogen gas on the cathode side. In Alkaline systems silica breakthrough can result in formation of potassium silicate in the electrolyte solution, resulting in a shortened interval for solution replacement.

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Additional Parameters

Trace Metals: The presence of metals in trace concentrations (parts per trillion or nanogram per liter) are typically first detected with low-range conductivity measurement. Metals include Iron, Copper and Boron at ppt levels can contribute to fouling of catalyst-coated exchange membranes (PEM) and electrodes (Alkaline), resulting in undesired galvanic corrosion and shortened replacement intervals. This is a particular concern for electrolysis systems that use catalysts in limited supply (such as iridium). The presence of iron may contribute to fluoride release (from membrane deterioration).

Acid or cationic conductivity: In the deionization stage of water preparation channeling occurs over time in resin beds. Conductivity drift after deionization stage is generally an indicator that reins beds have reached the point of exhaustion and need recharge. Standard direct conductivity has a 'noise' level as water purity approaches the lower limit of 0.0555 µS/cm. Cationic conductivity serves to 'amplify' the measurement; continuous monitoring provide an earlier warning of resin bed exhaustion and additional reaction time for resin exchange before produced water becomes of specification.

Chlorine: Continuous chlorine measurement in water preparation stage protects reverse osmosis membranes. Prolonged exposure of RO membranes to chlorine exceeding 38 ppb (based on 1000 ppm-hr over three years) is detrimental to membrane structure and integrity, while absence of disinfectant promotes biofouling in membranes and causes loss of recovery.

Turbidity: The amount of suspended solids present in water is an essential quality indicator. Silt, sand, bacteria, spores, and chemical precipitates all contribute to the cloudiness or turbidity of water. As a result, turbidity monitoring is a critical tool for producing and maintaining the water used throughout the Green Hydrogen production process. From the very low turbidities of the exceedingly high purity water produced for use in the steam cycle, to the much higher turbidities of discharged wastewater, the right instrument is required. Turbidity can be measured both before and after mechanical filtration to make critical determinations of:

- Makeup water filtration requirements
- Potential for membrane fouling
- Corrosion monitoring
- Cooling water and wastewater quality

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Solutions for water quality monitoring of hydrogen production

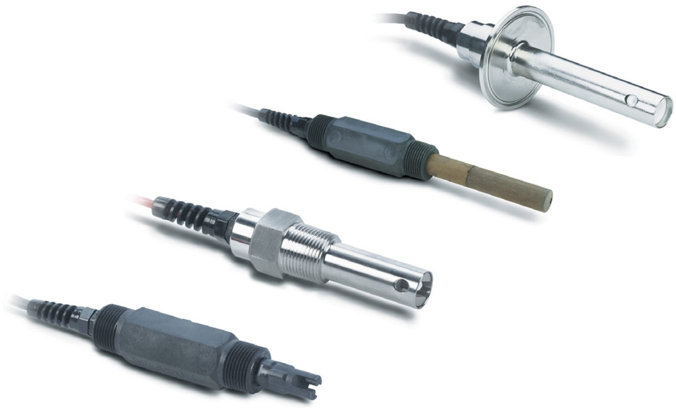
With more than 60 years as the leading expert in water quality analysis we leverage our global position and expertise in pure water quality to provide leadership and elevate our presence in emerging water-critical industries through commercial and innovation investment.

Hach® has the most comprehensive coverage of pure water quality parameters and a wide breadth of solutions for **electrolysis**, **process analyzers** and **sensors**, and **laboratory/field analysis** to support green hydrogen production.

Conductivity Sensors

Hach's contacting conductivity sensors measure a broad range (pure water 0.057 µS/cm up to 20,000 µS/cm) with high accuracy. Each sensor has a unique four-digit cell constant determined according to ISO 7888 and ASTM D 1125 standards.

Robust construction with 316 Stainless Steel and a sturdy industrial design ensures the product can withstand even the most demanding conditions.



9525sc Degassed Cation Conductivity System

An integral part of a complete ultra pure water analytics system, Hach's degassed cation conductivity (DCCP) system measures specific conductivity (SC), cation conductivity (CC), and degassed cation conductivity (DCC) and helps to reduce plant start-up time and distinguish between air and water contamination in pure water systems. This comprehensive approach saves time on design, installation, training, maintenance, and operation.

- **Reliable measurements**
- **Space-saving design**
- **Easy and safe handling**

pH/ORP

Hach offers a wide variety of process pH and ORP sensors to meet your application needs. The differential sensors use an innovative, unique electrode technology which results in greater accuracy, less drift, and less frequent calibration. The LCP sensors are designed to meet more rigorous industrial applications. And for those users on a budget, Hach offers a low cost line of combination pH/ORP sensors.

5500sc Silica Analyzer

Lower Maintenance, Less Downtime!

The 5500sc silica analyzer needs only two liters of reagent to perform unattended for up to 90 days.

The industry's only pressurized reagent delivery system eliminates the frequent maintenance associated with pumps. Grab Sample In and Grab Sample Out features allow quick analysis of a grab sample poured into the analyzer and facilitate taking a sample out of the online silica analyzer to verify in a lab test.

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NA5600sc Sodium Analyzer

Protect the metallurgy in your system and monitor for leaks at sub ppb. Our newest analyzer has a smaller footprint and uses the same interface as the 5500 sc.

- Automatic calibration
- Automatic electrode reactivation
- Optimum response time
- Reagent replenishment only every 90 days

TU5400sc Low range Turbidity

The new standard in the evolution of turbidity!

The TU5400sc employs a patented optical design that sees more of the sample than any other turbidimeter, delivering the best low-level precision and sensitivity while reducing variability between measurements.

- Ability to measure to 0.002 NTU, the next standard in the evolution of turbidity.
- Groundbreaking 360° x 90° Detection Technology
- Matching lab and online results

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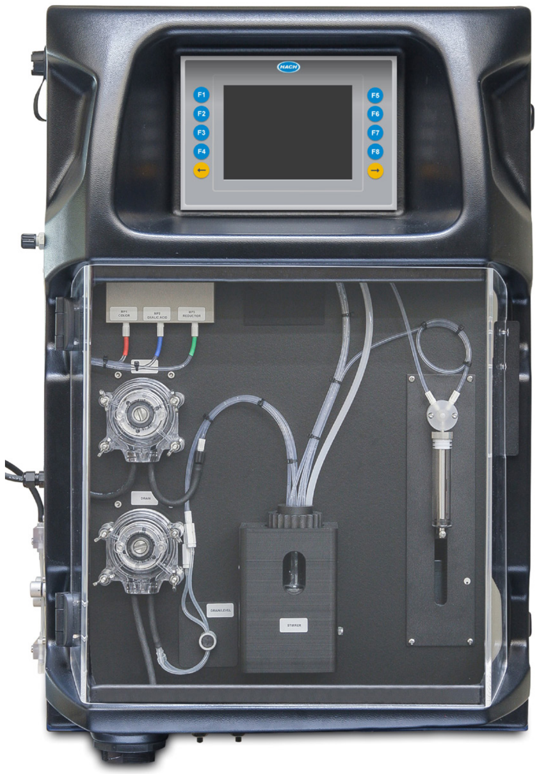
ULR CL17sc Ultra-Low Range Chlorine

Monitor and Optimize your Dechlorination Process!

Hach Ultra Low Range CL17sc has the lowest limit of detection at less than 8 ppb and uses colorimetric DPD Standard Method 4500-Cl G.

Understand the true impact of chlorine exposure. The Ultra-Low Range CL17sc allows for process control across your water cycle, including visibility into GAC exhaustion or channeling and dechlorinating agent dosage.

It is the only instrument with a cumulative chlorine counter, which helps you forecast your RO membrane efficiency and its useful life.



EZ Series Online Analyzers Your Complete Solution

One Platform – Multiple Technologies.

This versatile instrument platform makes it possible to match the online analysis to your established laboratory method.

EZ Series parameters cover water parameters such as:

- Trace metals like iron, copper, lead and manganese
- Microbial activity
- Alkalinity and hardness

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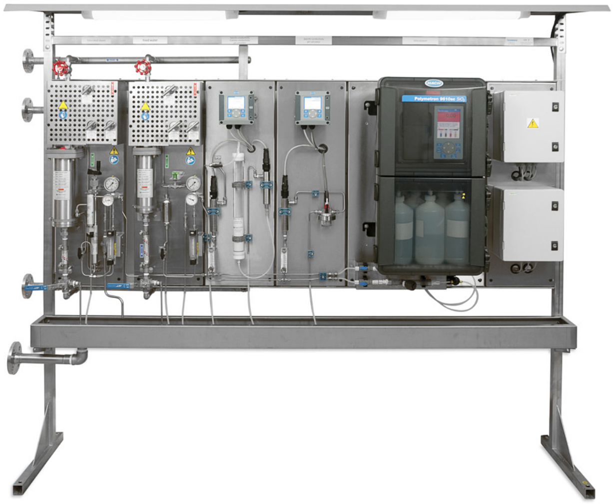
Water Analysis Panels

Water Analysis Panels are ready-to-use systems for sampling and online monitoring of water quality parameters in water preparation and electrolysis applications. The system provides precise, real-time knowledge about process status, and can be implemented in both automatic process control and security systems.

Industrial water processes may be extremely hot and under high pressure, requiring cooling and depressurization prior to online analysis or laboratory use. Flow rate must also be regulated to guarantee accurate, repeatable data.

Water Analysis Panels make it simple: install, connect the sample and cooling water, and start!



Conclusion

Hach has the knowledge, the solutions, and the proven track record to support the successful growth of green hydrogen production around the globe. Further, Hach will be there to service and support these operations in the years to come.

Hach Support Online (HSO) is a dynamic resource that delivers real-time answers, user-friendly search tools, multiple types of content, and easy ways to connect with Hach experts.

The Hach Training Center offers a large course catalog of workshop training, personalized training, and digital learning designed to increase proficiency and confidence for plant operators, instrument and field technicians, laboratory personnel, and plant managers and superintendents.

Hach ServicePlus® Programs have been developed to help solve your maintenance and support problems. Whether it's a lack of resources or skills, an instrument that is down, compliance concerns or the need for a predictive budget, we have programs to fit the unique challenges you face in your organizations.

To learn more, visit hach.com or reach out to a Hach representative today.

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DOC033.53.30768.Feb23

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