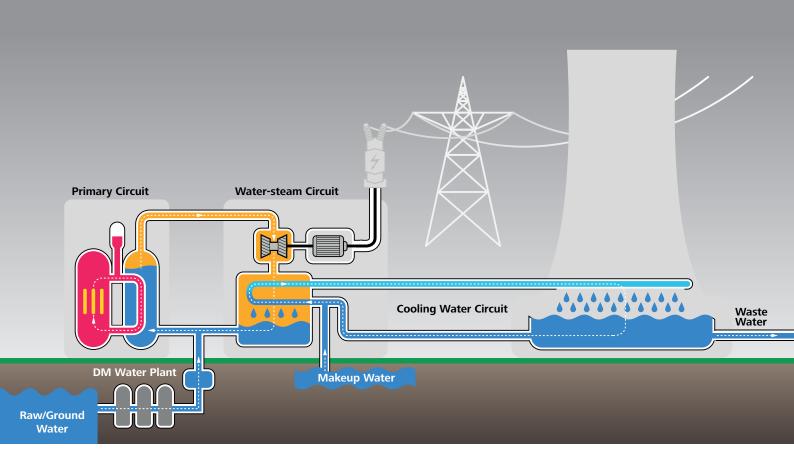
Dedicated Online Analyzers for Power Plants



Monitoring and Protecting against Corrosion



Power Plants & Corrosion

Nearly 50% of unplanned downtime in power plants is caused by contaminants or problems in the chemistry of the water-steam circuit, with corrosion being the primary factor. Corrosion chemistry monitoring helps to minimize loss of efficiency and protect the components coming in contact with steam and water against damage. The mechanisms and associated root causes responsible for most chemistry-related damage and efficiency loss are now very well understood, but the precise conditions at which corrosion and deposition activity begin are still not known. Past and present chemistry guidelines all serve to provide the operator with a warning as to when corrosion and/or deposition activities that place the power generation unit at risk may begin.

Various guidelines define the permissible operating ranges for water chemistry used by power plant operators, including standards provided by the Electric Power Research Institute (EPRI), the Association of Large

Boiler Operators (formally known as VGB – Vereinigung der Grosskesselbesitzer e.V.), the European Power Plant Suppliers' Association (EPPSA), and the International Association for the Properties of Water and Steam (IAPWS). Nuclear power generation is governed by the safety standards of the Nuclear Regulatory Commission (NRC) and the International Atomic Energy Agency (IAEA).

Every cooling circuit has a unique design and thus its own unique challenges. The specifics of the water chemistry to be regulated (and therefore the applicable limits) depend on the type of power plant, the cooling circuit design, and construction materials.

Timely and effective monitoring of power plant water chemistry is critical for maintaining efficiency and safety. By using online analyzers, operators gain the information they need to accurately identify trends and address operational issues before costly problems arise.

Dedicated Online Analyzers

Effective cycle chemistry programs depend upon the selection of treatments customized to the specific unit and its characteristics. Treatment control and optimization, in turn, requires rapid, accurate sampling and analytical capabilities. While all power plants can benefit from online analysis of critical parameters such as corrosion indicators and inhibitors for optimum chemistry control, monitoring of diagnostic parameters such as chloride, sodium, sulfate, ammonia, hydrazine, silica and TOC can also be highly advantageous for protection and process optimization. Not only do dedicated online analyzers help to safeguard plant operation and efficiency, but they also provide a continuous record of plant operating conditions for increased plant uptime and to facilitate long-term improvements in productivity.

Metrohm Process Analytics offers integrated online analytical systems based on lab-proven methods in titration, spectroscopy, electrochemistry, photometry, TOC, ion chromatography, and ion selective measurements. These application-specific solutions utilize optimized sample conditioning to bring precision and accuracy to effective power plant chemistry monitoring. This product line leverages Metrohm Applikon's expertise in online analysis and the know-how of the world leader in ion analysis, Metrohm AG, to bring laboratory analysis online for excellence in continuous monitoring and control.

Flow-Accelerated Corrosion Monitoring

Flow-accelerated corrosion (FAC) of the metal components in power plant water-steam circuits reduces the lifetime of water-exposed carbon steel pipework and copper heat exchangers. Zinc ions, phosphates, and phosphonates are commonly used as corrosion inhibitors in steel piping. Chloride causes pitting corrosion on turbine blades and rotors. In combination with

sulfate, it also leads to corrosion fatigue and stress corrosion cracking (SCC). To prevent these detrimental effects, power plants have to monitor these anions in the water-steam circuit to trace levels. Corrosive ions and the corrosion inhibitors can be monitored by ion chromatography.

Process Ion Chromatograph

The new Process Ion Chromatograph (IC) is designed for autonomous operation with absolute reliability, based on our decades of experience as a leader in this analytical technique. The Process IC allows multicomponent analysis from a single sample stream, providing important information about any corrosion event. The Process IC measures multiple anions and/or cations simultaneously, and offers further measurement options including monitoring multiple sample streams, corrosive ions, dissolved metals, and corrosion inhibitors. Providing quick, reliable results, this system gives valuable insight into the status of corrosion processes within a plant by continuous comparison of results with control values. By correlating the results with specific events, effective corrective action can quickly be undertaken to prevent or minimize plant downtime.

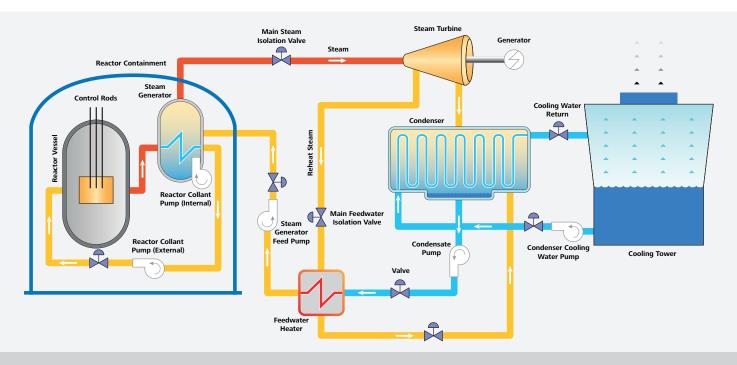


| Purpose | Corrosion monitoring & control, increased infrastructure lifetime |
|----------------------------|---|
| Application | Online monitoring of corrosive ions and corrosion inhibitors |
| Technology | Ion Chromatography |
| Concentration Range | ng/L to % |
| Sampling | Metrohm Inline Sample Preparation (MISP) |
| Analysis time | Application-dependent, typically 10–45 minutes |

Nuclear Power Plants

The most common types of nuclear reactors are the boiling water reactor (BWR) and the pressurized water reactor (PWR). The primary circuit of a PWR circulates cooling water at high pressure (up to 160 bar) through the reactor core, where boric acid dissolved in the primary circuit acts as a moderator for the nuclear reaction. Determination of boric acid concentration in the primary circuit is thus extremely important in controlling reactivity for reactor efficiency and safety.

Fuel assemblies cannot be exchanged during operation of a PWR due to their use of light water, so a fuel reserve must be in place prior to the start of an operating cycle. The associated excess activity in the reactor is controlled by using a higher boric acid concentration. As the fuel decays, the boric acid level is lowered to maximize reactor output, achieved via dilution with ultrapure water. From one refueling to the next, boric acid concentration fluctuates from 2,000 mg/L to zero, and thus online monitoring of boric acid concentration in the primary circuit is extremely important for efficient and reliable operation.



The Boric Acid Process Analyzer provides fast and reliable values via potentiometric titration for continuous monitoring of boric acid concentration throughout the fuel cycle, both during the process and in the spent fuel pool. Use of an automated titration system eliminates the tedious pipetting of the sample, distilled water, and mannitol solution needed for boric acid determination through manual methods. Automated analysis improves accuracy, eliminates the potential for operator error, and provides more rapid process feedback to maximize operational efficiency.

| Purpose | Safe operation | |
|----------------------|---------------------------------|--|
| Application | Online monitoring of boric acid | |
| | concentration | |
| Technology | Potentiometric titration | |
| Concentration | 0-6000 mg/L boron | |
| Range | | |
| Sampling | Fixed volume burette | |
| Analysis time | 1–15 minutes | |
| Enclosure | NEMA 4/IP66 standard, Class 1, | |
| | Div. 2 enclosure optional | |



Uranium Analyzer

Control and treatment of liquid effluents are required throughout uranium mining and processing for effective environmental protection. Effluent water from nuclear power plants must also be monitored to ensure residual uranium concentration is within regulated limits. The Uranium Analyzer accurately determines uranium concentration in various water cycles and in waste water streams. Based on colorimetric measurement and available in both basic and advanced configurations, these systems provide sensitive detection of trace uranium concentrations. By integrating this online system into a plant, reporting of out-of-limit uranium can be made both rapidly and accurately.

| Purpose | Environmental protection |
|----------------------|---|
| Application | Online monitoring of uranium in water cycles and in waste water |
| Technology | Colorimetric measurement |
| Concentration | 0–100 mg/L uranium |
| Range | |
| Sampling | Constant |
| Analysis time | 10 minutes |

Fossil Power Plants

Fossil power plants consume fuel such as coal, natural gas, or oil, generating electricity via a steam turbine. The steam generation process requires cooling water, either in a closed loop or open loop system, so that the steam can be condensed for either re-use or discharge depending on the type of system. Cooling water composition must be monitored to optimize power generation, ensuring plant efficiency and safety. Additionally, exhaust gases containing carbon dioxide and sulfur dioxide produced during the power generation process must be treated prior to release to the environment. Monitoring of the flue gas treatment process is required both for plant efficiency and to ensure environmental compliance. Metrohm Process Analytics offers process analyzers based on tried and true laboratory methods for each of these applications to ensure safety, productivity, and environmental protection.

Flue gas Desulfurization Plant

The flue-gas desulfurization (FGD) process is used during the incineration of waste materials – one of the steps in the process to remove species that are deemed harmful to the environment. FGD is a well-established process technology in fossil-fuel power plant operations.

Calcium Analyzer

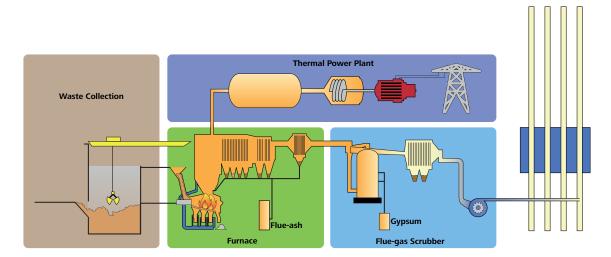
Flue gas is treated with an alkali to remove sulfur dioxide, typically using calcium hydroxide, or less frequently magnesium hydroxide, both of which react within the sulfur reduction process with sulfate and neutralize the acid content and precipitate as FGD-gypsum. One of the final products of the neutralization and reduction process is sulfate, which in turn will form calcium sulfate, or magnesium sulfate. The Metrohm Process Analytics Calcium Analyzer is based on both potentiometric and thermometric titration techniques, and is used to measure both the calcium hydroxide and sulfate content in several stages of the scrubbing process. By utilizing these online measurement approaches, the efficiency of the scrubber can be optimized for process performance and scale formation can be prevented, resulting in reduced operational and maintenance costs.



| Purpose | Environmental protection and process efficiency |
|------------------------|---|
| Application | Online monitoring of calcium hydroxide |
| Technology | Potentiometric and thermometric titration |
| Concentration Range | Ca ²⁺ 0–40 g/L: SO ₄ ² - 0–100 g/L |
| Sampling | Filtration to remove solids |
| Analysis time | 10–15 minutes |

Benefits of Metrohm Process Analyzers

- Process analyzers that provide automated analysis results
- Analytics based on industry standard lab methods
- Optimized sample conditioning for automated and reliable operation
- Easily transfer lab methods online to reduce method bias
- · Rapid, accurate results maximize safety, efficiency and



When flue gas is treated with a scrubbing solution, acidic CO_2 is reversibly chemically bound by amines in the solution, after which it is released by heating and then compressed, dried, and liquefied. After the amine-containing scrubbing solution has been cleaned by counter flowing steam, it is cooled and recycled back into the process. The Carbon Capture Analyzer determines the CO_2 binding capacity of the scrubbing solution that is required to completely remove the CO_2 in the flue gas from measured bound and free CO_2 concentrations in the scrubbing solution.

A single Carbon Capture Analyzer can monitor several sample streams and determine the ${\rm CO_2}$ binding capacity of several amine scrubbers in succession. By implementing Metrohm's fully automated online monitoring solution for this process, it is possible to optimize the amine activity and measure the efficiency of the ${\rm CO_2}$ capture, reducing overall costs while ensuring environmental compliance for ${\rm CO_2}$ emissions.

| Purpose | Process efficiency and environmental protection |
|----------------------------|--|
| Application | Online monitoring of CO ₂ binding and amine concentration |
| Technology | Potentiometric titration |
| Concentration Range | 0–100% CO ₂ , 0–100% amine |
| Sampling | Filtration, density – used for concentration determination |
| Analysis time | 15–20 minutes |

Cooling Water Cycle

Cooling water is used to condense the exhaust steam from the turbine to water, traveling through kilometers of piping in the condenser before being sent back to the water-steam circuit as feed water. The cooling water itself is cooled either by once-through cooling, in which heat is transferred to water taken from a river, or in a circuit in a wet cooling tower via heat dissipation into the atmosphere. Continuous circulation of the cooling water in either system increases the concentration of contaminants, and requires water analysis to control corrosion and deposition processes taking place in the cooling water circuit. Metrohm Process Analytics online process analyzers provide sensitive and reliable determination of contaminants at the low concentrations present in cooling water to enable rapid feedback and corrective action.

Ammonia is added to cooling water streams to help maintain a slightly basic pH, thus slowing corrosion. Other nitrogen containing corrosion inhibitors such as azoles are sometimes used, which can degrade to produce nitrogen species such as ammonia, nitrite, and nitrate in water streams. Monitoring of many nitrogen species is required prior to water and waste water discharge to ensure environmental compliance. While a more basic nitrogen analyzer can be used for monitoring a specific nitrogen species such as ammonia, the Nitrogen Species Analyzer delivers rapid, accurate measurements of ammonia, nitrite, and nitrate species simultaneously, and can be configured to handle multiple streams.

| Analysis time | 10 minutes |
|----------------------|---|
| Purpose | Corrosion prevention and environmental protection |
| Application | Online monitoring of ammonia and other nitrogen species |
| Technology | Ion-selective electrode or colorimetry |
| Concentration | Ammonia: 0.15–50 mg/L by |
| Range | ISE (other ranges possible) or 0.003–3 mg/L by colorimetric method, Nitrite: 0–5 mg/L by colorimetric method, Nitrate: 0–20 mg/L by colorimetric method |
| Sampling | Filtration |
| Analysis time | 10 minutes |





Silica Analyzer

Buildup of silica from boiler feed and cooling water can lead to reduced boiler efficiency and eventually blockage and rupture of pipes. Monitoring of the silica content in influent and cooling water can provide valuable information that is useful in preventing scaling and operational efficiency losses. The Metrohm Process Analytics Silica Analyzer can monitor silica levels from low ppb to high ppm level, which is critical for maintaining the required low levels of silica and preventing costly scaling and related issues.

| Purpose | Scaling prevention |
|----------------------------|-----------------------------|
| Application | Online monitoring of silica |
| Technology | Colorimetry |
| Concentration Range | 0–1 mg/L silica |
| Sampling | Filtration |
| Analysis time | 10 minutes |



Phosphate Analyzer

Trisodium phosphate is used for corrosion prevention in boiler water systems, leading to the need to monitor phosphate levels at several points within the process. Phosphate levels are ideally kept low to prevent any precipitation and solids transport, yet must remain high enough for corrosion prevention. The phosphate used for this purpose can sometimes be carried over into other systems, particularly the steam system, leading to similar precipitation and scaling issues.

| Purpose | Corrosion prevention, scaling | |
|----------------------|-------------------------------------|--|
| | prevention, and environmental | |
| | compliance | |
| Application | Online monitoring of free phosphate | |
| Technology | Colorimetry | |
| Concentration | 0.01-0.5 mg P/L | |
| Range | | |
| Sampling | Filtration | |
| Analysis time | 10 minutes | |



www.metrohm.com



