Keeping corrosion at bay

Analysis in ultra-supercritical power plants

Corrosion is the natural enemy of steam-electric power plants, eating away at pipes, turbine blades, and rotors. The lack of a separation between gas and liquid phases in supercritical power plants means that corrosive anions can enter the water-steam circuit without hindrance and cause severe damage as a result. Their concentrations therefore have to be monitored at all times, right down to the ultratrace range. With exactly this purpose in mind, five new ultra-supercritical units belonging to the Taiwan Power Company are being equipped with Metrohm ion chromatography systems.

Finding the right solution to the problems of energy that the world faces still seems a distant goal. Nuclear energy is too dangerous, renewables are both too expensive and too inefficient, and fossil fuels are too dirty. As things stand, around 80% of the world's energy is supplied by fossil fuels – petroleum, natural gas, coal, and peat[1] – and given the low levels of efficiency demonstrated by conventional power plants (around 36%), this represents a considerable burden on the environment. Supercritical and ultra-supercritical power plants go comparably easy on fuel resources and the environment, thanks to their improved efficiency which can reach up to 45%. However, they place particular demands on analysis.

Online IC Monitoring from Metrohm is up to this challenge. At two of its Taiwan sites, the Taiwan Power Company is planning to expand its coal-fired power plants to include three ultra-supercritical 800-megawatt units in Linkou, and two in Talin. These are scheduled to go into operation between 2016 and 2021 – and will feature Metrohm IC systems.

Steam-electric power plants in theory

In the first stage of a steam-electric power plant, a feed pump is used to convey water into the steam generator, where it is then heated and vaporized by fuel heat (produced by burning coal, for example). The steam that arises from this process is pressurized. It expands through a turbine whose mechanical power is eventually converted into electrical power by a connected generator. Once released, the steam moves into a condenser, where it is cooled by cooling water and returned to its liquid state. The water can now be reheated, and the cycle begins again. Figure 1 shows a diagram of the two-circuit system (water-steam circuit and cooling water circuit) that takes place in a steam-electric power plant.

The theoretical Clausius-Rankine cycle describes the ideal steam-electric power process. This assumes that all changes in the water's state take place without any losses and are reversible – specifically, this refers to the heating in the steam boiler, steam expansion in the turbine, heat removal and condensation in the condenser, and compression of the liquid water by the effect of the feed pump. Based on the description of the Clausius-Rankine cycle, it is possible to deduce how efficiently a circuit is operating. This is affected by factors such as the steam pressure and temperature: The higher the pressure and temperature of the live steam, the higher the thermodynamic efficiency.

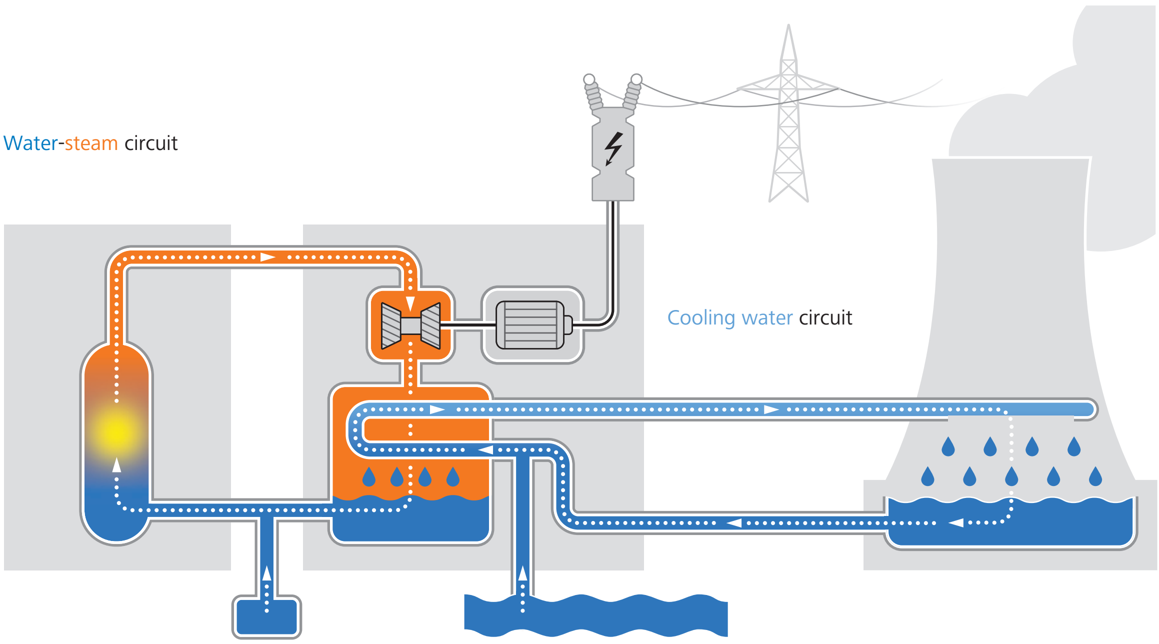


Figure 1. The two-circuit system shown here is made up of the water-steam circuit and the cooling water circuit. Water is pumped into the steam generator (on the very left), where it is heated. The steam then migrates through the pipe system to the turbine and drives this, producing electricity. In the condenser, the steam condenses by emitting heat energy to the cooling water. Following this, the water is fed back into the steam generator and the process begins again.

Steam-electric power plants in practice

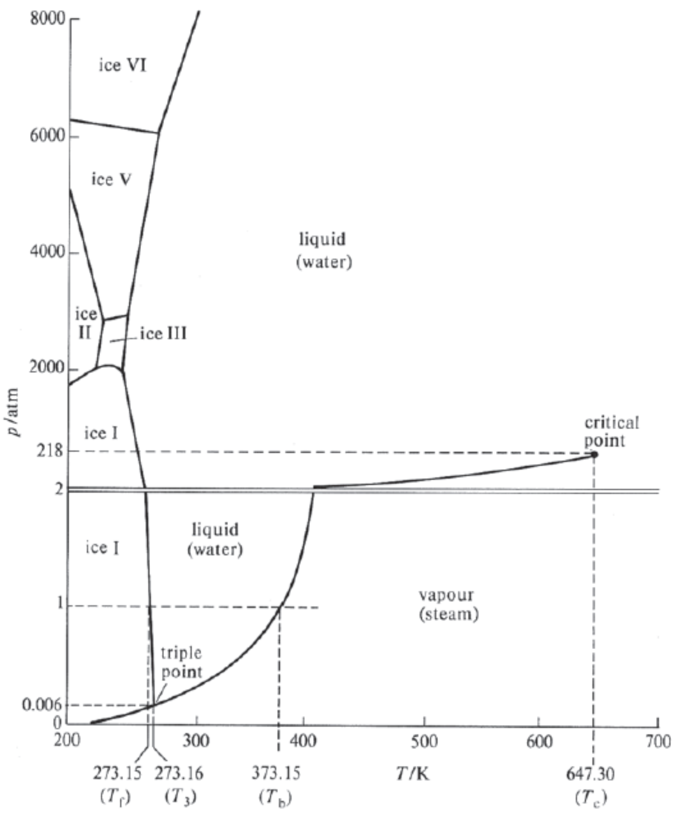
The actual steam-electric power process has to contend with something else that affects efficiency levels, however: energy losses. One example of these are leakage flows, which are flows of steam that pass by the turbine but do not actually help to drive it. As a result, the theoretical efficiency level derived from the Clausius-Rankine cycle remains an unattainable goal in reality.

Supercritical power plants

Regardless of this, it is still possible to improve efficiency in a steam-electric power plant by increasing live steam parameters. Specifically, raising the pressure and temperature of the steam leads to a higher level of efficiency, exactly as the Clausius-Rankine cycle suggests. Power plants whose temperature and pressure exceed 374 °C and 221 bar respectively are referred to as supercritical power plants.

Supercritical water is a term used in cases where the water exceeds what is known as the critical point – that is, the point on the phase diagram whose temperature and pressure coordinates are 374 °C and 221 bar (Figure 2). Generating steam under supercritical conditions does not form the gas bubbles that are seen during vaporization under subcritical conditions. There are no coexisting gas and liquid phases; instead, this is replaced by a supercritical fluid that has the density of a liquid but the viscosity of a gas. If the critical pressure and temperature levels are significantly exceeded – something which takes place in the coal-fired power plants being built today, for example – then this setup is referred to as an ultra-supercritical power plant.

The supercritical water that is generated during the first stage in the water-steam circuit is released through the turbine. Once this has happened, the pressure will once again have dropped below the critical point. In the condenser, the water is cooled further by the cooling water circuit, thus returning it fully to its liquid form.



A sensitive analysis technique is a must: the required detection limits are up to a hundred times lower than in subcritical power plants.

Figure 2. The phase diagram of water. If water exceeds the critical point at approximately 374 °C (647.30 K) and 221 bar (218 atm), it reaches a supercritical state. Source: P. W. Atkins, Physical Chemistry, 2nd ed., 1978, p.193

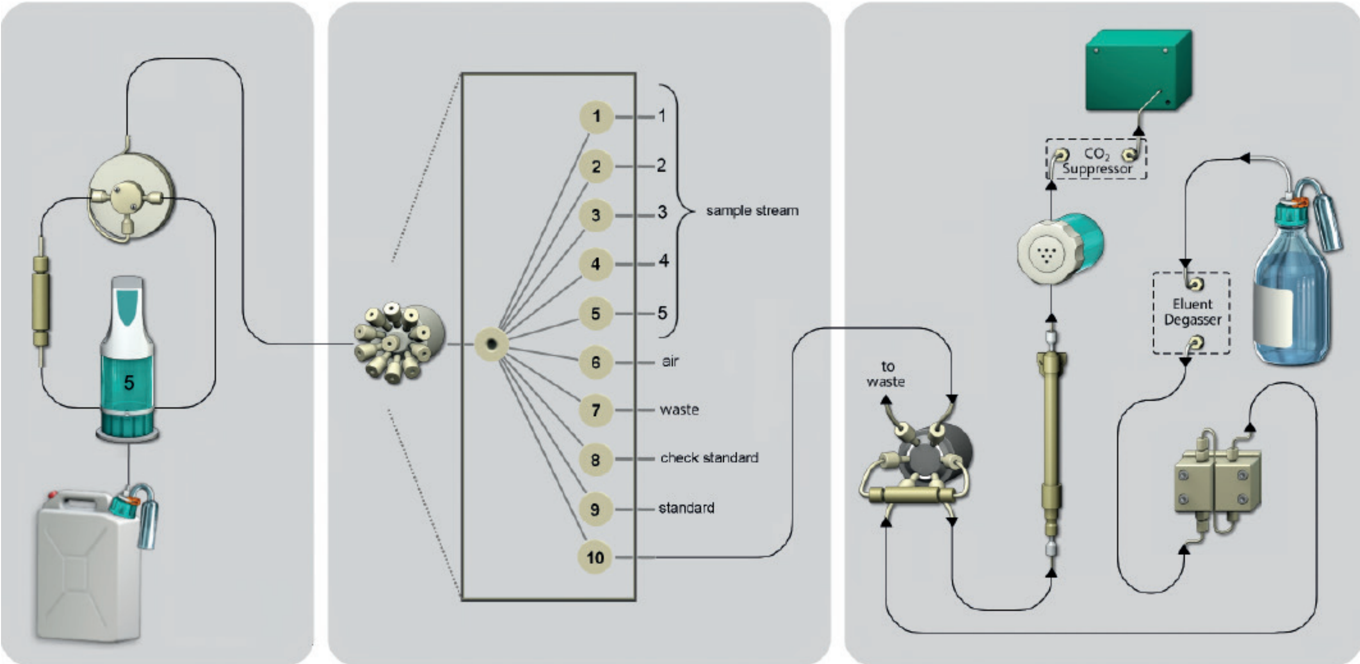


Figure 3. Diagram of the Metrohm IC system for online determination of chloride and sulfate traces in the water-steam circuit. It is possible to monitor five freely selectable sample streams alternately. The 10-port selector valve provides further connection points for both the calibration standard and the check standard.

Exacting inspections to prevent corrosion

Unlike subcritical power plants, supercritical plants do not feature a drum in which the steam and liquid phase are separated from one another. This means that any contamination in the boiler feed water can enter the water-steam circuit and attack its components, resulting in increased deposit and corrosion levels; one example of this is the pitting corrosion that turbine blades and rotors can experience when exposed to chloride. Combined with sulfate, chloride can also cause corrosion fatigue and stress corrosion cracking. Vaporous ammonium compounds exacerbate these effects.

Corrosive anions have to be monitored at all times. Since even traces can have devastating consequences, it is essential to use an analysis method that is appropriately sensitive – in other words, accommodating detection limits of 0.5 to 5 µg/L, up to a hundred times lower than in subcritical power plants. Precise, reliable measurement in the ultratrace range requires the processes to be automated as much as possible.

IC: A solution to rely on

Metrohm offers a complete solution for this task: Online IC Monitoring featuring combined Inline Preconcentration and Inline Matrix Elimination (Figure 3). The online analysis takes place in the process itself, and no sampling is required as the analysis system is fed directly and continuously with samples via a bypass in the process – in this case, at the water-steam circuit. This enables continuous monitoring.

In some power plants, phosphates are added to the boiler feed water in order to prevent corrosion. Phosphates form corrosion-resistant protective films on metal surfaces, and cracks and defects are phosphatized in their presence. For this reason, it is often necessary to determine the phosphate concentration in the boiler feed water. This is a task that Metrohm IC takes in its stride, too.

Metrohm IC in Taiwan

Metrohm IC systems will be a feature of the five new steam-electric power units at the Linkou Thermal Power Plant and the Talin Thermal Power Plant, analyzing water at various points in the water-steam circuit.

Before the chromatography itself takes place, the chloride and sulfate ions are preconcentrated. This preconcentration process and matrix elimination, as well as the conductivity detection that takes place after sequential suppression, enables analyte determination to be carried out using a technique that is both highly sensitive and reliable. Figure 4 shows the chromatogram of an artificial sample that contains chloride, sulfate, and phosphate.

Summary

Supercritical and ultra-supercritical power plants require analysis techniques to meet specific demands. The conditions that prevail in the water-steam circuits of these plants are extreme. The high levels of pressure and temperature make the components in the circuits susceptible to corrosion. For this reason, substances in the boiler feed water and steam that promote or inhibit corrosion have to be monitored at all times. Ultratrace analysis of these substances requires technology that delivers the appropriate level of sensitivity – and when it comes to online monitoring of chloride, sulfate, and phosphate, Metrohm ion chromatography featuring Inline Preconcentration and Inline Matrix Elimination is a perfect choice. It is performed both directly in the process and fully automatically.

References

[1] http://www.iea.org/publications/freepublications/publication/KeyWorld2013.pdf

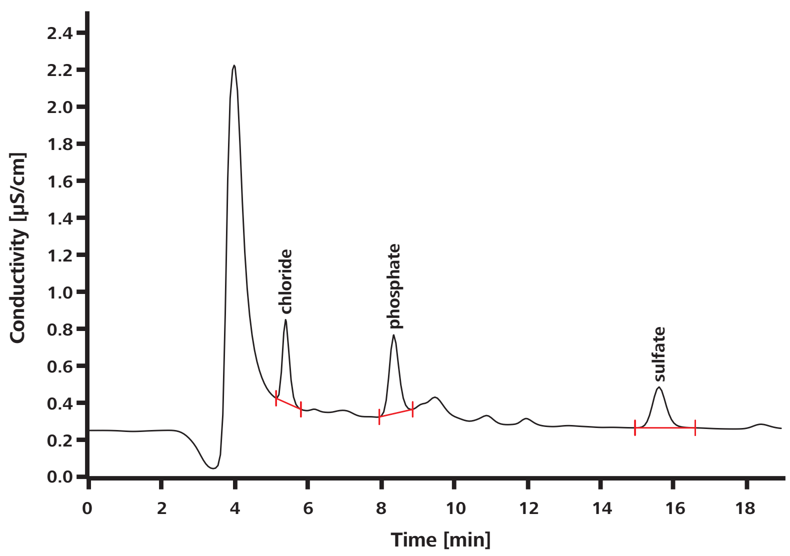


Figure 4. Artificial sample from the water-steam circuit of a supercritically operated reactor, with 1 µg/L chloride, 3 µg/L phosphate, and 1 µg/L sulfate added to it; column: Metrosep A Supp 10 - 100/2.0; eluent: 5 mmol/L Na_2CO_3, 5 mmol/L $NaHCO_3$, 0.25 mL/min; column temperature: 45 °C; preconcentration volume: 4,000 µL