

# The Economic Benefits and Goals of Power Plant Chemistry

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## ABSTRACT

Thus far, the chemist in a power plant has quite often been regarded as a necessary evil or as inevitable costs. The purpose of this paper is to explain the economic benefits of a chemist, the need to have a specialist on the operation team, the purpose and goals of the job, and the expectations of the chemist from the power plant management's point of view.

Of course, the economic impact, the possible risks, and (monetary) damage that might arise if the job is not done as it should be are discussed here as well.

This paper concentrates on the goals and purpose of the chemist's activities regarding the water/steam cycle and the components therein. Future papers will also deal with the chemist's footprint on the cooling system, including the cooling water make-up system, the flue gas path, and the treatment of other systems and machines.

## INTRODUCTION

Independent of the actual changes in the energy market and technologies, water/steam cycles will be needed and present for many years in the future, because the type of heat source (e.g., green hydrogen, etc.) does not have any major influence on the chemical issues on the water/steam side. Consequently, good plant chemistry will also be urgently needed in the future, which means we all have to maintain and increase our knowledge and foster the development of experts in this area.

The chemistry department in a power plant is responsible for numerous tasks. Usually, the chemistry department is responsible for releasing the annual environmental report.

In addition to these regulatory, administrative tasks, the chemist in a power plant is in charge of controlling and maintaining the water and steam qualities necessary to operate the boiler and turbine. This is also the case for the various cooling systems and other water qualities required, such as service water, demineralized water, flue gas cleaning, scrubbing make-up, etc.

If the given parameter limits for the various streams are exceeded, the management does not only expect the chemists to raise their hand and call attention to the deviation. In these cases, the plant chemist is similar to a physician,

meaning it is expected that a clear "diagnosis" together with a clear "therapy" will be presented to the plant management and the operators. In other words, useful, efficient, fast, and economic proposals are to be made on how to return to normal operation values in the shortest possible time. Quite often, it is outside the chemist's responsibility to fix the problem as such, which requires that specialists from other fields become involved.

The aforementioned list is by far not complete. Depending on the location, type, and design of the power plant (sea water cooled, dry cooling towers/air-cooled condenser, nuclear, fossil, combined cycle, industrial power plant, etc.), many other tasks might fall within the area of responsibility of the chemistry department. Nevertheless, the abovementioned list already gives an impression of the different and varied challenges the chemist in a power plant faces every day.

This paper will concentrate on the goals and purpose of the chemist's activities regarding the water/steam cycle and the components therein. Future papers will also deal with the chemist's footprint on the cooling system, including the cooling water make-up system, the flue gas path, and the treatment of other systems and machines.

## GOALS AND PURPOSE OF POWER PLANT CHEMISTRY WITH A FOCUS ON THE WATER/STEAM CYCLE

The chemist supports the operators of water/steam cycles in power plants and related systems in selecting and judging suitable water regimes in respect to a safe and economically sound operation of the power plant over a long period of time.

Within this given framework, the objectives of power plant chemistry focus primarily on protecting and retaining the asset value of the water/steam cycle and the components, apparatuses, and machines therein and of course the environment as well. Furthermore, power plant chemists are able to determine the source of changes which are caused by the chemical processes, and which affect the working fluids and the power plant components in terms of their performance under operating conditions.

They are also able to identify both the desirable and the undesirable chemical processes that can occur during power plant operation, as well as their effects on efficiency, availability, and reliability, and their long-term consequences. Based on this, the most suitable conditioning and monitoring strategy needs to be developed and implemented. In case of deviations, the chemist

advises on and implements countermeasures to return to the desired conditioning and monitoring regime within the predefined limits for the chemical parameters.

A good plant chemist fulfils three major and indispensable tasks [1]:

- routine chemistry
- strategic chemistry
- troubleshooting chemistry

In a nutshell, the chemist's activities are aimed at preventing corrosion and/or scaling so that the planned service life and availability of the power plant can be assured by means of optimized chemical treatment and monitoring, recognizing undesirable corrosive reactions at an early stage, and counteracting them by taking the appropriate remedial action.

This means that the power plant chemist is (or at least should be) able to recognize processes that are likely to cause an accelerated degradation or aging of the power plant and initiate the appropriate counteraction. Of course, this objective requires that the chief chemist is empowered to do so by the plant management.

Figure 1 gives an overview of the various activities the power plant chemist should carry out in a combined cycle power plant (CCPP) [1].

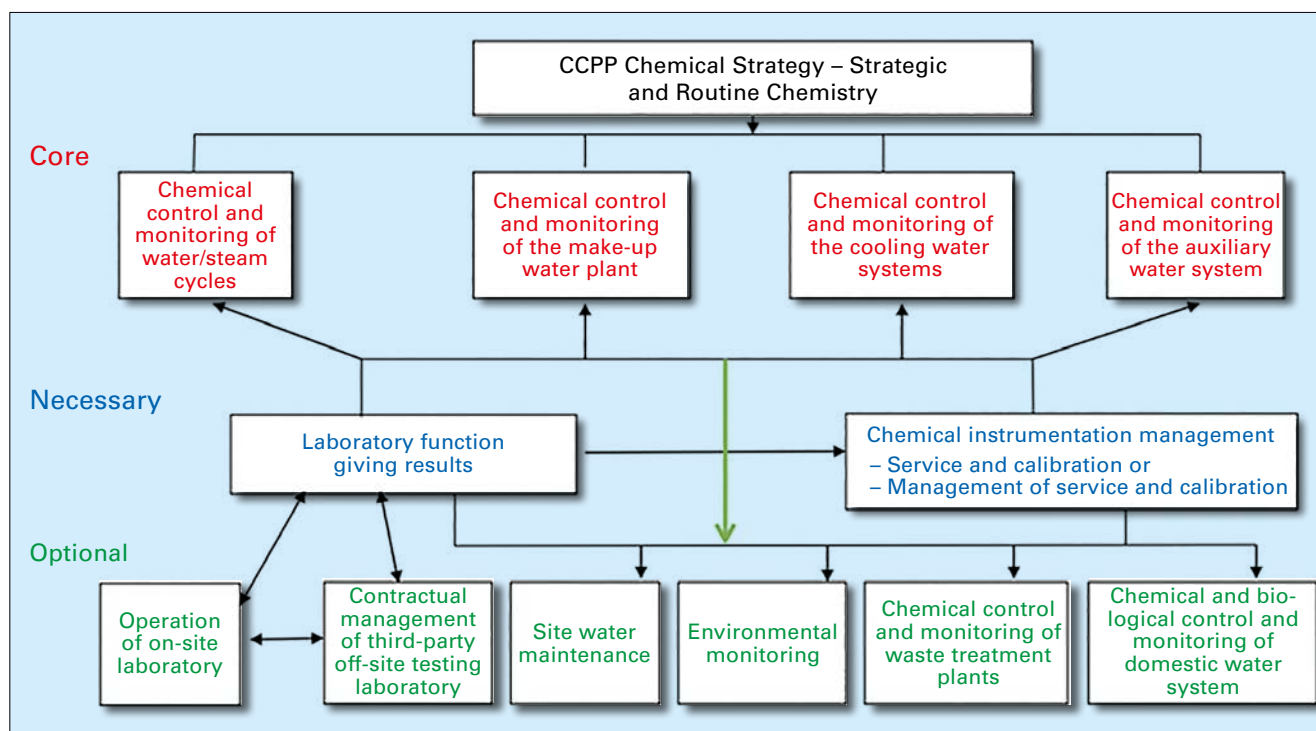


Figure 1: Core, necessary, and optional activities of the power plant chemist in a combined cycle power plant (CCPP) [1].

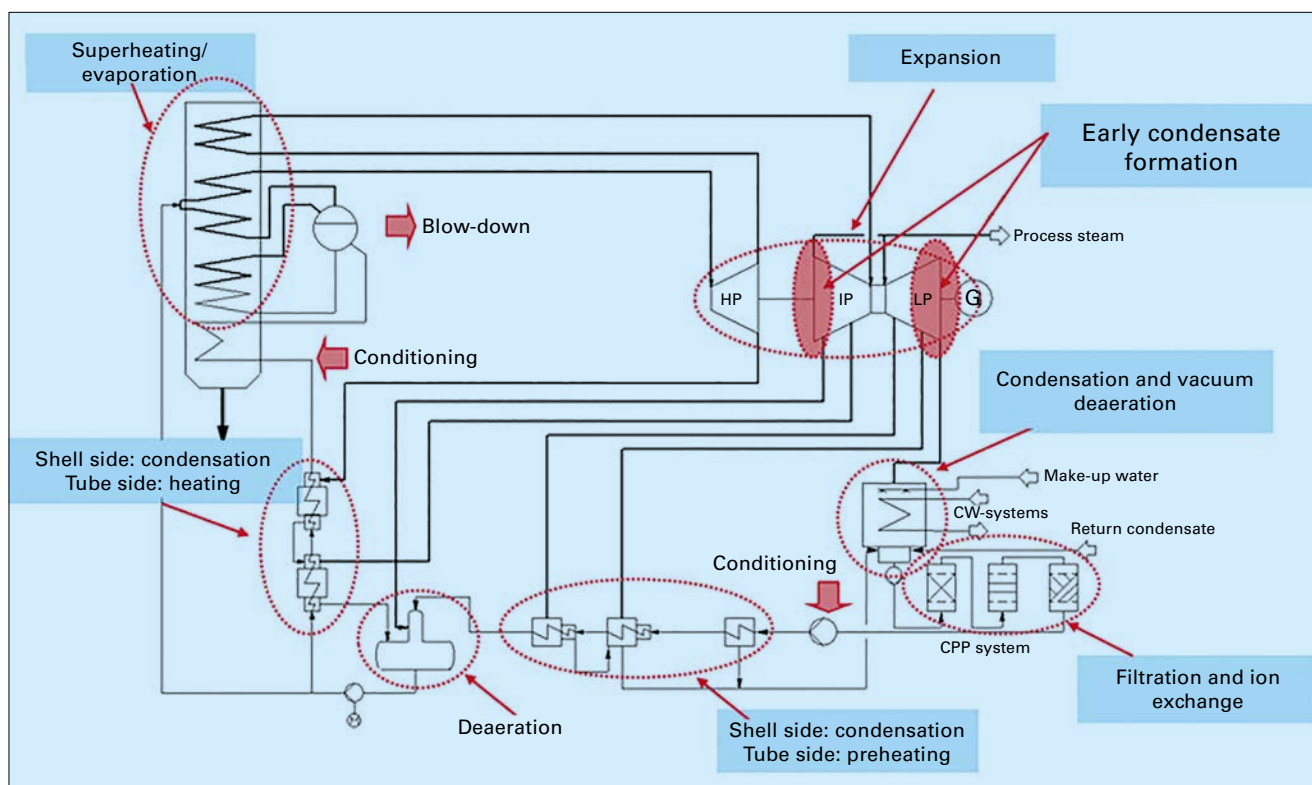


Figure 2:  
Schematic of the chemical and physical processes in the water/steam cycle.

CW cooling water

CPP condensate polishing plant

To be able to meet all expectations, goals, and targets, the knowledge of the person in charge of power plant chemistry is key. Since the chemistry in every water/steam cycle is always and without exception dependent on and correlated with the various processes integrated in the cycle, the power plant chemist must have a comprehensive and profound understanding of the chemical and physical processes that the working media water and steam (including conditioning chemicals and dissolved and undissolved unwanted impurities therein) undergo whilst circulating in the system; the chemist must also know and understand the individual system details and the interaction between the various materials the system is composed of and the working media in order to fulfil this task.

Figure 2 illustrates the sometimes complex interrelationships and chemical and physical processes and influences the working media water and steam, including the conditioning chemicals and undesired dissolved and undissolved impurities, undergo in the water/steam cycle.

Let's have a closer look into the water/steam cycle and the processes and changes that the working media undergo therein, starting at the

condenser. In the condenser, the wet steam with some ten to fifteen percent wetness coming in from the low-pressure (LP) turbine is condensed completely. The condenser usually operates at vacuum pressure, depending on the temperature of the cooling medium used. To enable efficient condensation, there needs to be continuous extraction of non-condensable gases. These gases come into the water/steam cycle with the make-up water (e.g., oxygen and nitrogen) or are formed in the water/steam cycle by chemical reactions of the working media water and steam or the conditioning chemicals under the influence of heat. For example, during the Schikorr-reaction (formation of magnetite from the interaction of water with iron) hydrogen is released, or gases may result from the reactions with or thermal degradation of dosed conditioning agents.

As the condenser usually operates under vacuum, the concentration of volatile conditioning chemicals as well as carbon dioxide is also reduced because at low temperature and low pressure less of these species can dissolve in the condensate. The deaeration in the condenser at vacuum conditions is very often more efficient

than the deaeration in the feedwater tank at elevated temperatures and higher pressure. This is the reason why in large power plants the make-up water is sprayed into the condenser instead of the deaerator on top of the feedwater tank. Depending on the tube material used in the condenser and the conditioning philosophy applied, copper or iron might be released into the condensate as well. In case of condenser leaks, air or cooling water can pollute the condensate.

If the unit supplies steam to a consumer for heating purposes, the return condensate from the consumer is usually returned into the condenser. Potential impurities might come into the system from there as well, which might make it necessary to install extra monitoring for continuous checking of the return condensate quality. Depending on the nature of the potential impurities, special filtration/polishing or rejection of the return condensate might be necessary.

It is the job of the station chemist to monitor all these processes and potential disturbances using suitable online analysers and in addition by taking grab samples for lab analyses.

If the power plant unit has a condensate polishing plant (CPP system), the condensate is purified and particulates as well as dissolved impurities are removed from the working medium. However, the CPP system can also act as source of pollution if the regeneration of the ion exchange resin that is usually used for purification is done incorrectly. The release of sodium can be a consequence. Monitoring and control of the clean condensate quality is also part of the chemist's job.

Downstream of the CPP system, conditioning chemicals need to be added to the clean condensate to adjust the pH value to the desired levels, at which corrosion of the materials used in the water/steam cycle is minimal. The station chemist is responsible for the selection and proper application of the most suitable conditioning chemicals, including maintenance of the dosing and sampling skids that are needed to form a closed control loop for this purpose. The selection of the conditioning chemicals and the determination of the target values for pH and oxygen – that is, the conditioning philosophy – need to consider not only the materials used in the water/steam cycle but must also include aspects of the operation, design, environment, and staff experience and knowledge, to mention just the most important factors.

In the LP preheaters, the condensate is preheated by the use of condensing steam. Depending on the tube material used in the LP preheaters, iron or copper (oxides) might be released into the condensate. To minimize such corrosion reactions, the pH and oxygen concentration (i.e. the redox potential) need to be monitored and if necessary adjusted to achieve the desired values. At the end of the day, the target values for the aforementioned parameters are always a compromise when it comes to mixed metallurgy installations. On the shell side, extraction steam from the steam turbine condenses. Consequently, two phases are present and if the chemistry is not adjusted and controlled well, flow-accelerated corrosion (FAC) might be the bad consequence.

During load changes, the condensation zone shifts within the preheater, which might result in mobilization of scale and deposits that might have formed during the previous operation period. For more details on what happens during steep load changes and low load operation in the entire water/steam cycle, see [2].

In the feedwater tank, the water is deaerated thermally. The chemist can control the deaeration efficiency by opening or throttling the valve in the pipeline that releases the exhaust of the deaerator/feedwater tank over the roof. However, via this path, some of the conditioning chemicals get lost as well, which might make it necessary to dose extra chemicals into the suction line of the feedwater pumps.

Usually before the feedwater enters the high-pressure (HP) preheaters, attemperator spray water is extracted for temperature control of the superheated steam. The quality of the spray water needs to meet the requirements of steam purity. Otherwise, the steam quality will be jeopardized, and precipitation of unwanted substances injected with the spray water might occur, which can lead to corrosion and/or tube ruptures or turbine failures. Assuring that this requirement is met, of course, is also part of the chemist's job.

In the HP preheaters, processes similar to those in the LP preheaters occur. Whilst the condensate for preheating in the LP preheaters is usually returned into the condenser hotwell or pumped forward into the feedwater tank, the HP preheater condensate is returned into the feedwater tank. The tubes of the HP preheaters are normally made of high chromium alloyed steel. Nevertheless, iron oxides can also be released from the heat exchangers into the water/steam

cycle by various corrosion mechanisms. It needs to be noted here that the steam and condensate used for preheating represents a separate internal cycle, wherein steam and preheating condensate circulate. Since part of the LP preheater condensate and all the HP preheater condensate is not routed back into the condenser hotwell and therefore does not pass through the CPP system, this portion of the working medium is never purified, which finally leads to the accumulation of impurities in the entire water/steam cycle. All this requires attention by the station chemist as well.

Leaving the HP preheater train, the feedwater enters the boiler by first passing through the economizer, where the feedwater is heated up to nearly boiling temperature at pressure. Attention is required from the chemist to detect potential FAC risk, which might happen in particular under special load conditions. This can be mastered with regular determination of the total iron content downstream of the economizer and in the boiler water. If abnormally high iron concentrations are measured, countermeasures like elevated pH adjustment, oxygen dosing, and additional (temporary) dosing of alkalizing chemicals directly in front of the economizer might be necessary.

The evaporator section of a drum boiler forms another internal loop wherein the boiler water circulates. In the evaporator not only part of the boiler water evaporates, but together with the water volatile conditioning chemicals as well as volatile impurities go over into the steam phase. This might result in depletion of, for example, ammonia in the boiler water, which shows a very high volatility, especially at low pressure. As a consequence, the pH of the boiler water may drop, and it might be necessary to add non-volatile chemicals to re-tune the pH. Depending on the recirculation rate, non-volatile species that come into the boiler with the feedwater concentrate in the boiler water. The evaporator system of a drum boiler might be regarded as a purification system and sink for non-volatile impurities that can be controlled by adjustment of the blow-down rate.

In addition to these physical processes, chemical reactions happen in the boiler as well. Because of the high temperature, silica that eventually enters into the water/steam cycle in colloidal form mainly with the make-up water (the quantity depends on the demineralization technology applied in the make-up water plant: ion exchange, reverse osmosis, electrodeionization, or a combination of these) is digested to form silic-

ic acid. The volatility of silicic acid is pressure dependent. The higher the pressure, the more silica will be dissolved in the steam. Other species, for example organic matter that is easily removable in the make-up water system, might decompose as well and form long and short chain carbonic acids. The final break-down product is carbon dioxide, which is not that dangerous in terms of corrosiveness for the materials used in the water/steam cycle, and especially in the boiler and turbine section of it. This however does not hold true for other break-down products on the way down to CO<sub>2</sub>. Formic acid, acetic acid, and others are also at least in part volatile and are very aggressive corrodents, especially in the area of first condensation at the LP turbine.

Additionally, break-down products of organic impurities might cause boiler water foaming, which makes it almost impossible to assure a good steam and water separation. Therefore, in case of organic impurities in the boiler water, one might always consider and check for boiler water carry-over. How to do this is described very well in the respective International Association for the Properties of Water and Steam (IAPWS) technical guidance document [3].

What happens in the superheater now? The saturated steam is further heated, and the remaining small portion of water droplets is evaporated. All the impurities that were dissolved in these water droplets will dry out and might precipitate on the inner tube wall surfaces of the superheater tubes or be dragged with the steam flow onto and through the turbine. Organic components that have come into the steam might further decompose to form additional organic acids, which play an important role in the early condensate in regard to the pH of the first condensate droplets. We will come to this later.

In the HP turbine, the steam loses part of its enthalpy and is expanded, and the temperature and pressure of the steam drop. Some species that have been dissolved in the steam at higher pressure might exceed the saturation point and form precipitation on the turbine blades. A good example of this process in the HP turbine is the formation of copper deposition.

Usually, the expanded steam is returned into the boiler and reheated there. The temperature of the reheated steam leaving the boiler again is controlled with the help of attemperator spray water injection. Again, the requirement is that the spray water quality needs to be similar to the steam quality requirements. Otherwise, precipitation, formation of deposits, and corrosion



might be the result. The additional heat impact of course might lead to further decomposition of organic impurities in the steam.

From the reheater of the boiler the steam is routed into the intermediate-pressure (IP) turbine. Further enthalpy reduction and pressure and temperature drop take place, which can again lead to precipitation of substances that have been dissolved in the steam. Silica is a good example of deposits that form in the pressure and temperature range in which the IP turbine is operated. [Figure 3](#) shows silica deposits on IP turbine blades.

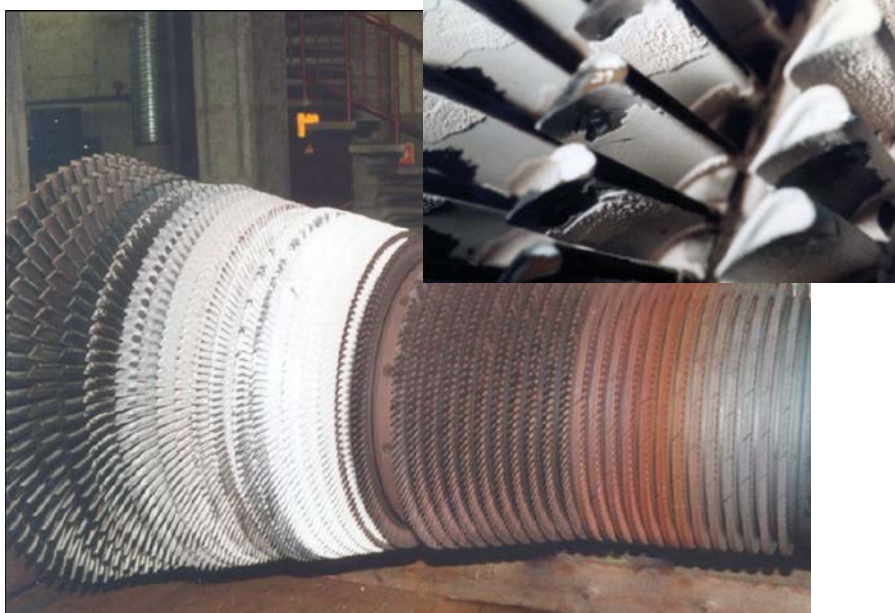


Figure 3:  
Silica deposits on an IP turbine.

At the unit in Figure 3, the make-up water plant was unable to remove all silica from the raw water and the chemist failed to control the silica content in the boiler water by opening the blow-down valve to avoid excess silica in the steam. The intention to save water and energy in this way turned out to be misguided as the silica precipitation on the turbine blade surfaces caused a tremendous efficiency, and thus monetary, loss. In addition, the removal of the deposit required a weeklong outage with opening of the turbine casing and mechanical cleaning of the blades by blasting, which together with the lost revenues and profit equalled financial losses in the million-dollar range.

At the LP turbine now, the steam is further expanded down to vacuum pressure. At the so-called Wilson line, the first condensate droplets appear. Because of the substance-specific distribution coefficients, this early condensate shows an acidic pH if ammonia is used as a volatile alkalization chemical. The higher the concentration of impurities and organic acids in the steam, the lower the pH of the early condensate. This phenomenon has been reported by Svoboda et al [4], for example. Of course, such acidic water droplets are also rich in salt, which means these droplets represent a strong acidic electrolyte that can easily cause corrosive attack on the turbine parts that are in contact with it.

All these chemical processes are fairly similar in combined cycles or so-called industrial plants as well.

All this shows that it is not sufficient to employ a classic chemist working in a laboratory environment, who looks at individual, selected measuring points or single areas. The current condition of the entire water/steam cycle in addition to that of the location where the sample has been extracted at the time of sampling must always be considered in the diagnosis, risk assessment, and also the recommendation of any measures.

This also makes it very clear that this can never be accomplished by other specialist engineers (e.g., boiler engineers), as they are already fully occupied with their very own activities in purely quantitative terms and are therefore unable to deal with this complex topic to the necessary extent and with the necessary depth of detail and due care.

Only with a sound knowledge of corrosion science and a clear understanding of the individual plant process(es) in addition to chemical expertise can diagnoses and risk assessments be carried out correctly and efficiently, thus ultimately enabling the entire power plant team, including management, to be advised correctly in chemistry-related issues.

Therefore, plant chemistry cannot be reduced to pure measurement or laboratory activities. The power plant chemist must always be in constant contact with the various specialists involved in the power plant operation and always be informed about the current status of the plant and the current activities. This also means that the chemistry department must provide additional

information on its own, for example through repeated and longer visits to the control room, in order to independently carry out the operational observations that are important for the chemical department. In this way it can take ad hoc corrective action at critical moments, for instance when the boiler is heating up.

In order to meet these requirements, a responsible chemist must be appropriately integrated into the power plant operational organization and also have a certain authority to issue directives in defined areas of competence. To fulfil this responsibility, however, this person must not only have chemical expertise in general, but also and especially know and understand the entire plant process to also be able to make the correct diagnoses and implement the measures to be derived from them. In other words, simplified monitoring activity with the help of laboratory staff does not fulfil this requirement in any case.

This is the only way to ensure that the minimum water chemistry requirements are safely achieved and maintained at any time of operation. For this purpose, too, it is necessary for the power plant chemist to have sufficiently precise knowledge of the plant-specific, process-technical details to be able to support the operators and management in the determination of measures and to advise them with regard to the setting of priorities.

In addition to the aforementioned process knowledge, this also includes continuity on site, so that current developments can be experienced directly and without delay or loss of information.

It is also clear that, as a rule, staff from an (outsourced) centralized laboratory, for example, does not meet these requirements, or at least not completely and in the required detail, especially if they only take samples on site for further laboratory analyses on request.

The necessary monitoring of the chemical parameters, which also includes the repeatedly necessary plausibility check of the derived values, can only be carried out by experienced chemical personnel. This monitoring requires full attention and therefore cannot simply be carried out "en passant". Consequently, it cannot be done by the technical operators in the control room either, as they are already occupied with other very important activities that require an equally high level of concentration and attention.

Dedicated experienced chemical personnel can, if necessary, assess the chemical situation with sufficient precision and speed and thus can also spontaneously and directly implement appropriate protective measures to avoid any risks.

## POTENTIAL RISKS, DAMAGE, AND ECONOMIC IMPACT OF INAPPROPRIATE POWER PLANT CHEMISTRY

Spectacular major losses caused by chemicals or malfunction and misoperation of chemical systems are only one side of the story.

One of the biggest losses that one of the authors has been involved in during root cause analysis and troubleshooting happened in the last years of his professional career at a coal-fired station in Germany. The brand new unit (an investment of nearly 1 billion euros) was wrecked within only 25 minutes due to a chemical accident whilst the water/steam cycle was operating at full load conditions. How could this happen? Obviously, the operators did not trust the readings and alarms coming from the steam and water analysis system (SWAS) and regarded them as not true, which finally led to incorrect conclusions and decisions that caused the disaster.

Damage to turbines caused by carry-over of caustic soda is not uncommon. It is well known that sodium hydroxide can cause stress corrosion cracking on turbine blades and other highly stressed components and parts. Crack propagation following this mecha-

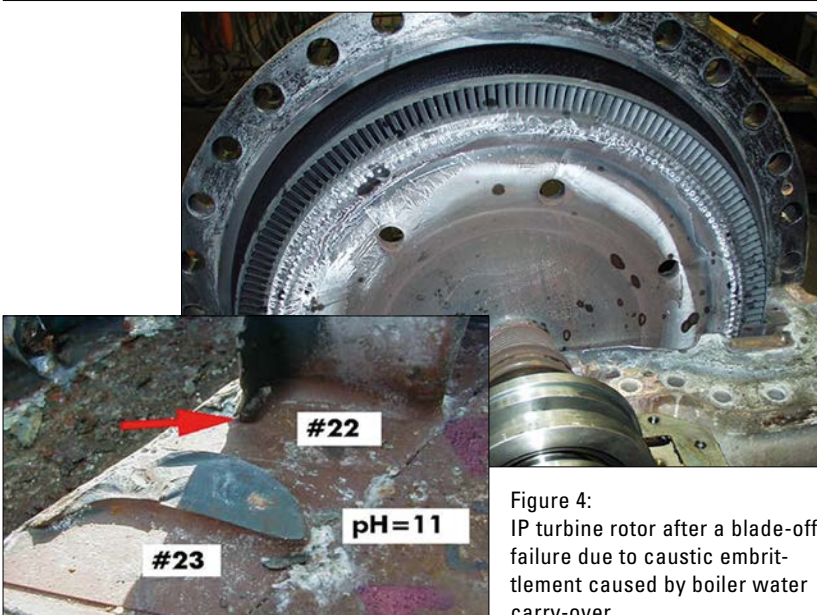


Figure 4: IP turbine rotor after a blade-off failure due to caustic embrittlement caused by boiler water carry-over.



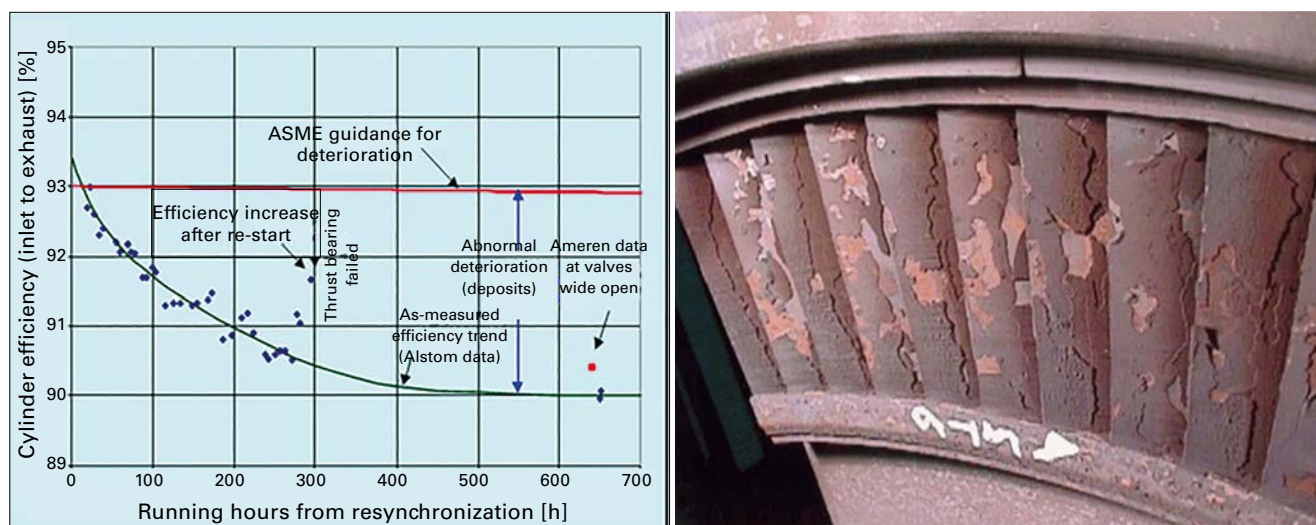


Figure 5:  
Effect of copper deposits on turbine blade surfaces.

ASME American Society of Mechanical Engineers  
Ameren Ameren Corporation, St. Louis, MO, USA

nism is very fast so that a blade-off can happen just hours after the intrusion of sodium into the steam. In [Figure 4](#) the rotor of an IP turbine is shown that suffered from blade-off caused by boiler water carry-over due to foaming of the boiler water after a cooling water in-leakage.

This damage could have been prevented if the operators in the control room had responded to the alarms generated in the sampling system in an appropriate way and time. However, quite often (as in this case), an action plan for alarmed deviation from the normal values of the chemical parameters in the water/steam cycle does not exist or the operators are not trained for such events. Thus, the chemistry alarms in this example were ignored for a certain time until the catastrophic blade-off caused such high vibrations of the turbine shaft that they led to an immediate automatic shutdown of the turbo-set.

A condenser leak that causes cooling water ingress can be detected easily if suitable online instruments are installed in the sampling system (for example, by online conductivity measurement of the raw condensate and alarming if the set high alarm value has been reached or exceeded). Boiler water carry-over can be detected by online monitoring of the saturated and/or superheated steam sodium content.

Again, it turns out that the repair costs plus lost revenues for the time of repair are by far higher than the costs for any sophisticated sampling system, elaboration of action plans for chemistry alarms, and (at least) yearly training of the operators.

Much more frequently, monetary loss is caused by non-optimized operation or conditioning / chemical treatment and suboptimal plant design. Of course, such losses are not as spectacular and not as costly as the examples above.

Almost no one is aware of how much money can be lost simply due to some deposition on the surface of turbine blades or scale in or on boiler tubes, which drastically reduces efficiency and may eventually cause boiler tube bursts due to overheating. To demonstrate this, [Figure 5](#) shows the impact of copper deposits on turbine efficiency [5].

As can be seen in the graph, copper deposition progresses quickly and can cause efficiency losses of more than 3 percentage points within only a few hundred hours of operation. For a 500MW unit this can add up to monetary losses in the multi-millions per year.

The question might arise whether the chemist in this case did their job well. Wouldn't it be possible to avoid such copper deposition? Yes, of course it would have been possible to avoid copper deposition simply if during the planning phase the choice had been made for the more expensive investment, for example for a condenser with stainless steel or titanium tubes instead of brass or cupronickel and stainless steel tubes for the LP preheaters instead of "cheaper" preheaters with copper or cupronickel tubes. Once the decision against all ferrous metallurgy is made, the chemist can only aim to minimize the release of copper from these heat exchangers by application and adjustment of the most



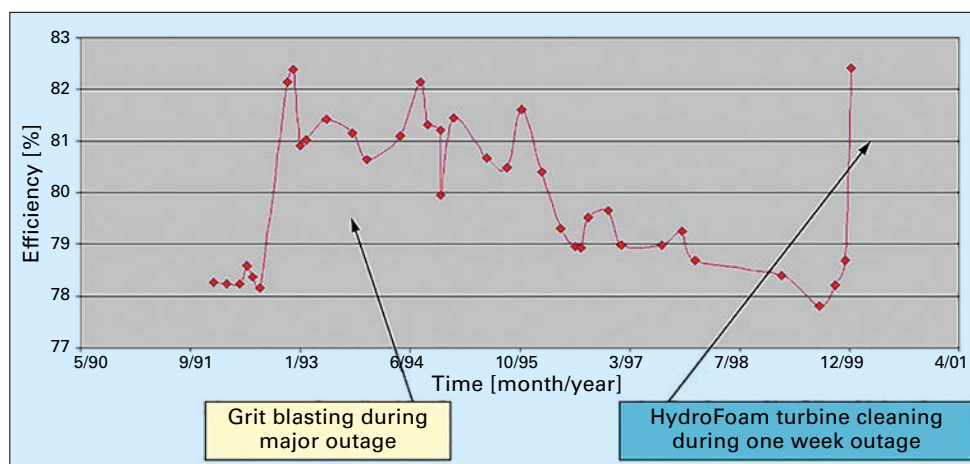


Figure 6: Effect of grit blasting and foam cleaning on turbine performance. Both methods restored efficiency equally successfully (diagram courtesy of Danny Foster).

suitable chemical regime in terms of desired pH and redox potential. This however will always remain a compromise between the most suitable chemistry for the components containing copper alloys and the optimum chemistry for all other parts made of steel.

When the copper has formed deposits on the blades, chemistry can help to remove it and regain efficiency. Foster and Trimble have reported impressively of the success in applying foam cleaning on turbines to remove copper deposits [6].

In Figure 6, the turbine efficiency degradation over time for a 270 MW steam turbine is shown. In this example, grit blasting during a major

overhaul could restore efficiency almost completely. However, as the copper release from the water/steam cycle continued to be an issue, the build-up of new deposits could not be avoided. The scatter in efficiency can be explained by the cleaning effects of condensing steam during cold starts, which washed off some of the deposits, and continuous precipitation during normal operation. Eight years after the major overhaul the efficiency degradation again reached an extent where it caused a million-dollar loss every year. It was decided to carry out a foam cleaning process on the HP turbine. As the graph shows impressively, the foam cleaning had a similar effect on efficiency restoration to that achieved by grit blasting.

## CONCLUSION

The primary goal and purpose of a power plant chemist is to prevent corrosion and deposition related failures in the power plant so that the plant is available to operate as and when required.

This is easy to say, but hard to do, because it requires not only the knowledge and know-how for proper execution of laboratory analyses in the trace area but equally good knowledge of process technology, chemical engineering, control systems engineering, materials science, and corrosion know-how, just to mention the most important areas of expertise. Not to be forgotten are also good communication skills and the ability to speak the managers' language.

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For many years he supported the technical committee "Chemistry" of VGB (a technical association of energy plant operators based in Essen, Germany) and gave essential input to standards and guidelines (e.g., S-010, S-006, S-116, and S-042).

He is also a member of the International Association for the Properties of Water and Steam (IAPWS) working group "Power Cycle Chemistry" and acted as the vice chair of this group for 2 years.

Since 2012 he has been lecturing at the Rheinisch-Westfälische Technische Hochschule (RWTH) Aachen University on power plant chemistry. Since 2013, Frank Udo has been an instructor for power plant chemistry issues for VDI (an association of German engineers) and since 2018 also for PPCHEM AG.

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