



IAPWS Technical Guidance on Power Cycle Chemistry Monitoring and Control for Frequently Cycling and Fast-Starting of HRSGs

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ABSTRACT

Because of the market situations in numerous countries worldwide, many combined cycle units require rapid startup and/or are cycled frequently (such as daily or twice daily start / stop). Under these conditions, there is minimal time for operators to prepare steam-water cycle on-line chemical sampling and monitoring equipment and to carry out chemistry checks. However, operators at most plants will still have to monitor steam purity to demonstrate that it is suitable for admission to the steam turbine with minimal delays to startup times. It is also critical that on-line chemical monitoring instrumentation is set up so that serious cycle contamination during startups can be detected and alerted to operators. To provide initial guidance towards addressing these issues, Technical Guidance Documents produced by the IAPWS Power Cycle Chemistry Working Group have now been updated to reflect the international consensus of experience in these areas. The key points are summarised in this update.

INTRODUCTION

Because of the market situations in numerous countries worldwide, many combined cycle units require rapid startup (i.e. able to have accelerated hot, warm and cold starts) and/or are cycled frequently (such as daily or twice daily start / stop). For example, fast-starting modern combined cycle plants can reach full load from gas turbine ignition in less than 30 minutes following a unit shutdown of eight hours or less (Figure 1). Under these conditions, there is minimal time for operators to prepare on-line chemical sampling and monitoring equipment and to carry out chemistry checks.

There are a number of aspects of steam-water chemistry monitoring at cycling and fast starting plants that operators need to consider. However, the two most important issues are:

- 1) How to monitor steam purity to demonstrate that it is suitable for admission to the steam turbine with minimal delays to startup times.
- 2) How to set up on-line chemical monitoring instrumentation to detect serious cycle contamination during startups.

Towards addressing these issues, the suite of Technical Guidance Documents issued by the Power Cycle

Chemistry Working Group of the International Association for the Properties of Water and Steam (IAPWS) have now been updated to reflect the consensus of experience in the Working Group in these areas. The key points are summarised in this update.

IAPWS POWER CYCLE CHEMISTRY TECHNICAL GUIDANCE DOCUMENTS

The IAPWS Power Cycle Chemistry Working Group has developed a suite of Technical Guidance Documents that provide international cycle chemistry guidelines for fossil and combined cycle/HRSG plants. These are:

- Corrosion Product Sampling and Analysis for Fossil and Combined Cycle Plants (2013);
- Steam Purity for Turbine Operation (2013);
- Instrumentation for Monitoring and Control of Cycle Chemistry for the Steam-Water Circuits of Fossil Fired and Combined Cycle Power Plants (2012);
- Phosphate and NaOH Treatments for the Steam-Water Circuits of Drum Boilers of Fossil and Combined Cycle/HRSG Power Plants (2011);

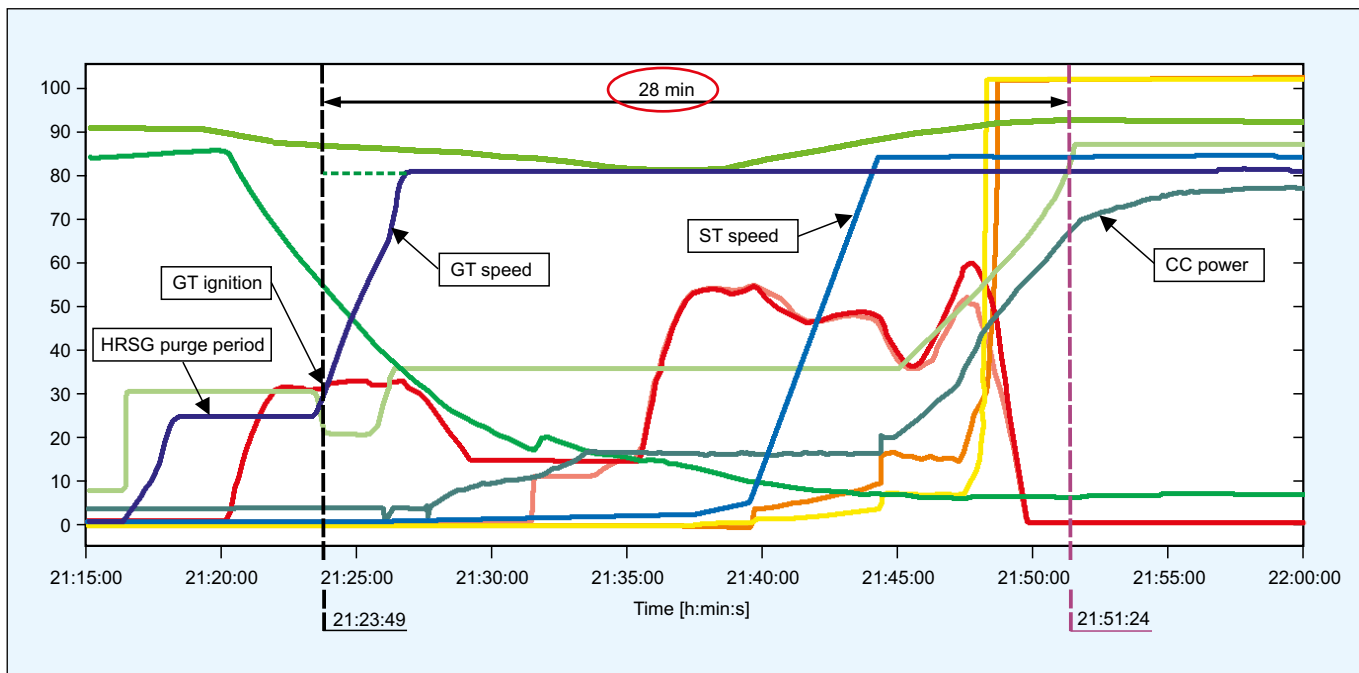


Figure 1:
Accelerated hot start of < 30 minutes achieved in field (courtesy of Alstom).

GT gas turbine
 ST steam turbine
 CC combined cycle
 HRSG heat recovery steam generator

- Volatile Treatments for the Steam-Water Circuits of Fossil and Combined Cycle/HRSG Power Plants (2010);
- Procedures for the Measurement of Carryover of Boiler Water into Steam (2008).

These documents are freely available and can be downloaded from the IAPWS website (www.iapws.org).

Three of these documents have been amended to cover the requirements for frequently cycling and fast starting of HRSGs: *Instrumentation for Monitoring and Control of Cycle Chemistry for the Steam-Water Circuits of Fossil Fired and Combined Cycle Power Plants*; *Phosphate and NaOH Treatments for the Steam-Water Circuits of Drum Boilers of Fossil and Combined Cycle/HRSG Power Plants*; and *Volatile Treatments for the Steam-Water Circuits of Fossil and Combined Cycle/HRSG Power Plants*.

For the Technical Guidance Documents that cover chemical treatments (phosphate, NaOH and volatile treatments), the 2015 revisions do not constitute significant changes to the guidelines for normal operation.

STEAM-WATER CYCLE CHEMISTRY MONITORING GUIDANCE FOR FREQUENTLY CYCLING AND FAST-STARTING OF HRSGS

Steam Purity Monitoring to Minimise Holds during Startups

In plants that are frequently started and for fast-start combined cycle plants, a key requirement is to have no chemistry holds during startup.

Whilst the acceptability of steam purity for admission to the steam turbine is usually demonstrated by the measurement of Conductivity After Cation Exchange (CACE), this will almost always be affected by air in-leakage (carbon dioxide) during shutdowns. During a startup, it then becomes important to be able to identify a condenser leak and distinguish contamination from air in-leakage (carbon dioxide), so that a relaxation of CACE limits can be adopted. However, without knowledge of the carbon dioxide levels in the cycle, it is not advised to relax the normal CACE limits for startup.

To achieve this, the additional measurement of Degassed Conductivity After Cation Exchange (DCACE) in superheated steam samples is suggested. This measurement provides useful additional information to distinguish air in-leakage from other forms of contaminant ingress so that a

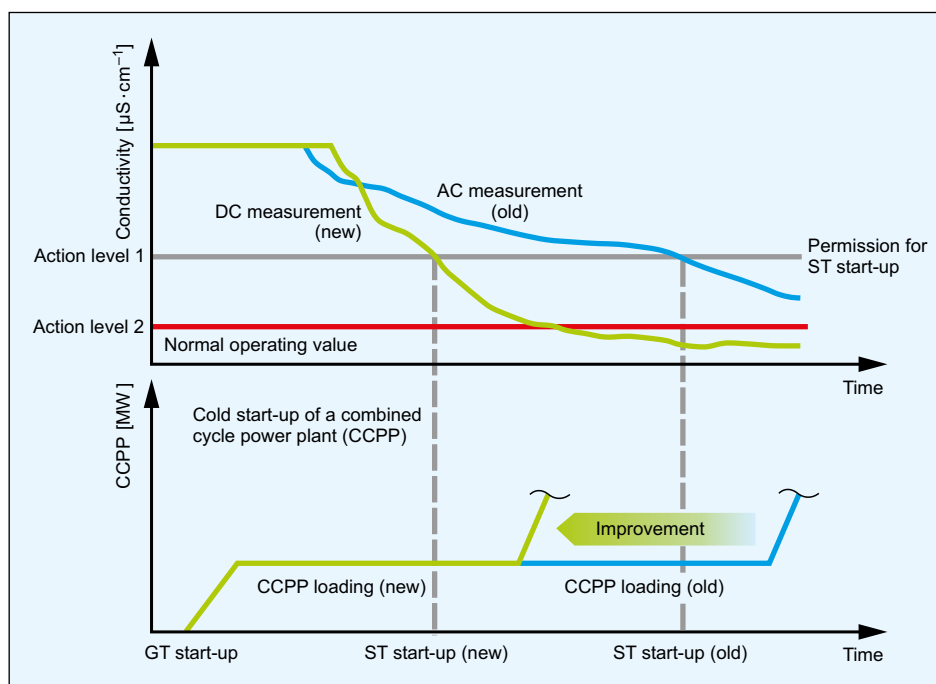


Figure 2:

Reduction in startup times with additional measurement of degassed conductivity after cation exchange (DCACE) on superheated steam (courtesy of Siemens).

DC degassed conductivity
 AC acid conductivity
 GT gas turbine
 ST steam turbine

relaxation in CACE associated with the former can be made to prevent delay in starting a unit (Figure 2). This aspect has also been covered in the IAPWS Technical Guidance Document for Steam Purity which provides guidance on the proper identification of carbon dioxide ingress.

On-Line Monitoring for Detecting Contamination during Startups

During startups, it is critical that the installed suite of on-line chemical monitoring instrumentation is able to detect any chemistry issues so that units can run when required. This is particularly important for water-cooled plants, especially those using estuarine or seawater, because of the need to detect condenser leaks at the earliest possible stage due to the potential for severe and rapid contamination and corrosion.

At fast-start and cycling plants, the emphasis for chemical sampling and monitoring during startups has to be to reduce the time needed to acquire correct and representative measurements and also for the installed suite of instrumentation to be sufficient for operators to be able to distinguish between air in-leakage or more serious contaminant ingress taking place. This may require new approaches to the physical location of sample analysers at plants, with additional instrumentation potentially also needed to provide adequate contaminant detection capability.

Irrespective of the running regime, monitoring of condensate (usually at the condensate extraction pump dis-

charge, CPD) is essential in all plants to provide the first warning of contaminant ingress as a result of condenser leakage, slippage of regenerant chemicals from the make-up plant, or contaminated condensate from a storage system. This location also provides an indication of air in-leakage. The point of measurement is normally the CPD because of the requirement for pressure in the sample line to be greater than atmospheric pressure.

For frequently started and fast-start combined cycle units, it is now suggested that analysers for the CPD are located as close as possible to the sample extraction point, rather than being routed to a combined steam / water (wet rack) room. In this case, the combination of short sample lines, local sampling conditioning and local analysers will assist in detecting contaminant ingress at the earliest possible opportunity.

For plants with water-cooled condensers, the continuous measurement of sodium remains a key instrument at the CPD for all plants except those with air-cooled condensers. For fast-start HRSGs, the most useful additional measurement in the condensate would be DCACE. Together with the other parameters measured at this location, this will give fast information on whether there is air in-leakage or ingress of more significant contaminants of concern taking place, such as chloride and sulphate from condenser leaks.

In some plants, especially for seawater cooled units, it is also recognised that it can be advantageous to include additional on-line chemical monitoring in the condenser hotwell to provide a fast response to contamination during shutdowns. This usually requires having to extract a sam-

ple against condenser vacuum, followed by local conditioning and analysis. Typical hotwell monitoring can include conductivity (i.e. specific or direct conductivity), CACE and sodium. At seawater cooled plants, conductivity probes may be installed directly in the hotwell at a number of points below the waterline to provide a coarse indication of a condenser leak, though the obvious disadvantage is that these probes cannot be routinely removed for maintenance. Within the IAPWS Working Group, most experiences with hotwell sampling stations were also problematic because of the difficulties of extracting a sample under vacuum, inconvenience of installations below condenser water levels and high levels of maintenance. Because of these issues, the preferred IAPWS guidance remains to monitor for contamination at the CPD with CACE, oxygen and sodium as key instrumentation.

To reduce the time delay for correct readings to be obtained from on-line chemical monitoring instruments during startups, there are also advantages for keeping key instruments on a continuous refreshing cycle with demineralised water during unit shutdown periods to keep the analyser working. Phosphate, silica, conductivity and CACE could all have demineralised water off-line flushing. This should not be applied for sodium probes because their sensitivity can be reduced if continuously flushed with high purity water. The highest priorities for this set-up are sample points with instruments that are used for condenser leak detection and for ensuring steam purity for turbine admission during startups.

Phosphate and Caustic Treatments

Carryover

In all plants, the concentrations of phosphate (when products other than only tri-sodium phosphate are used, e.g. blends of phosphate, proprietary blends, or congruent or coordinated phosphate treatments) and NaOH alkalisng chemicals in HRSG evaporator waters need to be carefully controlled so that excessive concentrations do not occur which could lead to caustic corrosion in the boiler or to the carryover of corrosive impurities into steam and damage to the superheaters and turbine.

The risk of carryover from boiler drums and superheater contamination requires added emphasis for fast-start and cycling HRSGs because of the potential for repeated incidents during frequent startups and fast load transients. When operating with any phosphate treatment or NaOH treatment, it is most important that carryover is measured on a frequent basis using sodium as the indicator to confirm that carryover rates remain below the normal design and/or commissioning value (in case of elevated carryover and the potential for corrosive impurities, such as chloride, to be present in the steam) and that sodium concentrations in steam remain below the requirement or

guideline (but not necessarily that the carryover is above the normal value).

In fast-start and cycling HRSGs, carryover tests should be completed and then checked on a more frequent basis over the full range of possible operating conditions at a plant (i.e. not limited to baseload or steady state operation) so that operators fully understand any conditions under which any increased carryover occurs, e.g. unit load and drum level. In doing so, it is also advisable to conduct a specific drum level test with varying drum water level while monitoring carryover and saturated steam parameters so that operators understand the influence of drum level on carryover rates. Guidance on the measurement of drum carryover is available in an IAPWS Technical Guidance Document.

Tri-sodium phosphate is not known to be corrosive in the turbine either as a deposit or in a liquid film. Therefore, because of the increased risk of carryover in fast-start HRSGs, phosphate treatment (at a sodium-to-phosphate molar ratio of 3:1) may be the treatment of choice in comparison to caustic treatment in order to reduce the risk of damage to steam circuits and steam turbines from stress corrosion cracking. It is again emphasised that operators must be careful if boiler water sodium-to-phosphate molar ratios are greater than 3:1 because of the risk of NaOH carryover into the steam.

Steam Purity

Use of only tri-sodium phosphate for phosphate treatment (i.e. sodium-to-phosphate molar ratio of 3:1) also has the advantage that a relaxation of sodium limits in steam is allowed as discussed in the IAPWS Technical Guidance Document on Steam Purity. This may be an important factor for frequently started and fast-start HRSGs depending on drum carryover behaviour.

It is emphasised that the relaxation does not apply to units dosing sodium-to-phosphate molar ratios greater than 3:1 because of the risk of NaOH carryover into the steam. No steam purity relaxation at all is allowed for NaOH treatment.

It is again worth repeating the importance of measuring carryover on a frequent basis when operating with NaOH treatment or any phosphate treatment in order to confirm that carryover rates remain below the normal value and that sodium concentrations in steam remain below the applicable requirement or guideline.

Chemical Dosing

Some optimisation of dosing procedures for NaOH and phosphate boiler water treatments may be necessary for plants with frequent startups in order to minimise carry-

over risks. This might involve not dosing during startups until conditions have stabilised and reliable on-line chemical monitoring measurements are available. However, routinely running for extended periods of time with insufficient caustic or phosphate in LP and IP HRSG evaporators could increase the risk of flow-accelerated corrosion (FAC) at some locations. Therefore, it is important that dosing regimes are established that aim to minimise the duration of any boiler water chemical excursions while recognising carryover risks during transient conditions.

Phosphate Hideout

Although phosphate treatment may be recommended for use in circuits with drum pressures of up to 19.3 MPa (2800 psi), there are numerous observations that phosphate treatment can be difficult to control above drum pressures in the range 10–10.5 MPa (1 450–1 500 psi) due to phosphate hideout and hideout return, particularly in vertical gas path (VGP) HRSGs. Fast-start and cycling HRSGs are expected to experience more frequent hideout and chemistry control problems because of the frequent changes to operating conditions and circuit pressures.

For fast start and frequently cycled HRSGs, there is a preference for phosphate treatment with TSP over NaOH treatment as a result of potential increased carryover risks. If there are hideout control problems with the use of phosphate treatments, this can in some cases be overcome by the use of NaOH treatment. Three caveats are needed in these situations: the first is that if only TSP is used as the chemical additive, there will not be any corrosion problems in the HP evaporators associated with hideout; the second is that the use of NaOH treatment always demands more frequent monitoring of carryover; the third is that if the problem is dryout rather than hideout (more frequently experienced in VGP HRSGs with poorer circulation), then there is a concern for corrosion with NaOH treatment.

All-Volatile Treatment

For HP evaporators operated with an all-volatile treatment (AVT) based on ammonia, it is important that there is very strict contaminant control because of the limited neutralising capacity of ammonia at temperature. The additional precautions against contaminant ingress advised previously should be strongly considered together with operation with a full level of IAPWS instrumentation for the particular unit.

The target pH for AVT during normal operation should be within startup limits prior to or very quickly after a startup. Where practical, consideration should be given to automating the dosing control of ammonia in order to minimise the duration of chemical excursions and the need for operator intervention during startups.

Carryover from boiler drums is equally important for circuits operated with an AVT chemistry as it is for circuits with phosphate and NaOH regimes. This is because it is important to avoid carryover and steam contamination with chloride with any treatment regime.

Corrosion Product Transport

For fast-start and frequently cycling HRSGs, increased levels of corrosion products (total iron) will be transported to the higher pressure circuits, particularly during startups. In HP evaporator/boiler circuits, this will increase the risk of deposition and potentially promote under-deposit corrosion (UDC) boiler tube failure mechanisms during unit operation, such as hydrogen damage and caustic gouging failures in drum units typically operating above ~8 MPa (~1 100 psi). Consequently, it is important that operators take steps to minimise corrosion product transport, which is indicated by the measurement of total iron concentrations. Measures for minimising corrosion product transport are described in the following sections.

Flow-Accelerated Corrosion

For cycling plants or plants running for extended periods at low loads, locations in HRSGs that will operate within an FAC risk range will change during different modes of operation with changing temperature profiles across the HRSG.

For existing plants, it is important that the risk of FAC is considered across all expected modes of operation and that mitigation options are considered accordingly, e.g. inspection programmes, cycle chemistry optimisation, or materials replacement with chromium alloys if FAC cannot be prevented.

For new build HRSGs, the design specification should include armouring all susceptible FAC locations (which should now be well understood) with chromium-containing tubing or piping material. Even further, for cycling plants or plants running for extended periods at low loads, all plant components and locations that will operate within an FAC risk range during all expected modes of operation with changing temperature profiles across the HRSG should be protected with chromium alloys.

Particularly for HRSGs where the LP evaporator acts as the feedwater storage tank for the higher pressure circuits or attemperator sprays, preventing FAC will also assist in minimising the transport of feedwater corrosion products into the higher pressure circuits.

Air-Cooled Condensers with Carbon Steel Tubes

An increasing number of plants worldwide are equipped with air-cooled condensers. These can act as significant

sources of iron oxide that can be transported into the HP evaporators of HRSGs. At present, condensate polishing is not universal on plants with air-cooled condensers. However, for fast-start or cycling combined cycle units with air-cooled condensers, a condensate filter should be installed to ensure that large amounts of iron do not transport into the boiler during frequent startups. Experience indicates that a 5 µm absolute condensate filter will keep the total iron in the condensate consistently less than 10 µg · kg⁻¹.

Layup Procedures

In fast-start and cycling HRSGs, it is of paramount importance that adequate shutdown protection is applied. This is because:

- During unprotected shutdowns, corrosion can quickly become a serious issue for plant integrity, reliability and availability.
- Adequate shutdown protection is also necessary to minimise the iron transported during startups which can be deposited in HP boiler/evaporator circuits, as stated previously.

Adequate layup procedures should be adopted to cover shutdowns of greater than 24 hours because of the risk of corrosion during longer periods of standing.

Layup protection becomes increasingly important at frequently started and fast-start HRSGs because of the frequency and duration of shutdowns. However, there is often a conflict between layup protection and being able to maintain plant availability, particularly during changing situations where short shutdown periods can change to longer shutdown periods and vice versa. Many plants may start only by demand of the grid, often at short notice, and less as a routine plan. Consequently, layup procedures need to be as flexible as possible.

Corrosion Product Monitoring

For any steam raising plant, the monitoring of total iron levels is necessary to determine if there is an effective cycle chemistry programme in place.

To ensure that samples are representative and comparable, sampling should usually be conducted during periods when the unit is at stable or repetitively similar operation, not at the same time each day, or at a time convenient to the operator or chemist. However, this will not necessarily account for iron transport during startups and transient periods, which are key periods for corrosion product mobilisation in fast-start and cycling plants.

There remains a general need in the power industry for a guidance document to assist operators at fast-start and

cycling plant in reliably monitoring iron levels during transient periods and in interpreting the findings. IAPWS is working on this but, until this is available, monitoring total iron levels using the current IAPWS guidance should be followed.

CONCLUSIONS

At frequently started and fast-start HRSGs, it is important that steam-water cycle chemistry monitoring enables any serious cycle contamination during startups to be identified, but does not unnecessarily restrict the required short time for return to service. Therefore, the emphasis for cycle chemistry monitoring at these units is to reduce the time needed to acquire correct and representative measurements and to be able to identify any chemistry excursions as soon as possible. This may need additional monitoring and control features to be considered.

Security of operation for these units will benefit from monitoring of condensate (at the condensate extraction pump discharge) with short sample lines and local sample conditioning and analysers, rather than routing samples to a central steam/water sample rack or room.

During shutdowns, automatic demineralised flushing water for critical on-line chemical analysers for condenser leak detection and for steam purity monitoring is suggested in order to reduce the time delay for correct readings to be obtained during startups.

To provide additional clarification between serious contamination and air in-leakage during startups, continuous on-line measurement of DCACE in the condensate and on superheated steam will be of benefit. The use of DCACE as a fundamental instrument on superheated steam can also allow a relaxation in CACE associated with air in-leakage (as distinct from more serious contamination) to minimise delays for steam purity targets to be achieved when starting a unit.

Carryover from boiler drums and superheater contamination is of particular importance for fast-start and cycling HRSGs because of the risk of repeated incidents during frequent startups and fast load transients. Carryover tests should be completed and then checked on a more frequent basis over the full range of possible operating conditions at plants so that operators fully understand the conditions under which any increased carryover starts.

In fast-start and cycling HRSGs, it is of key importance that adequate layup procedures are adopted to cover shutdowns of greater than 24 hours because of the risk of corrosion during longer periods of standing. However, layup procedures will often need to be as flexible as possible due to the variability of unit running regimes.

PARTICIPATION IN IAPWS ACTIVITIES

IAPWS welcomes scientists and engineers with interest in research, current developments and operational experience in the field of power cycle chemistry. People interested in IAPWS Power Cycle Chemistry Working Group activities should contact either the chairs of their IAPWS National Committee (see the IAPWS website for contact details), the Working Group chair, Michael Rziha, michael.rziha@ppchem.com, or the IAPWS Executive Secretary, Dr. R. Barry Dooley, bdooley@structint.com. People do not need to be citizens or residents of member countries to participate in IAPWS working groups.

THE AUTHORS

Barry Dooley (B.S. with first class honors, Metallurgy, Ph.D., Metallurgy, both from University of Liverpool, U.K., D.Sc., Moscow Power Institute, Moscow, Russia) is a Senior Associate with Structural Integrity Associates. Before joining Structural Integrity Associates he was a Technical Executive, Materials and Chemistry, at the Electric Power Research Institute (EPRI) in Charlotte, North Carolina, where he managed the Cycle Chemistry, HRSG, and Materials Programs, as well as the Boiler Tube Failure Reduction/Cycle Chemistry Improvement and FAC Programs. Before joining EPRI in 1984, Barry Dooley spent nine years with Ontario Hydro in Toronto, Canada. From 1972 to 1975, he was a research officer in the Materials Division of the Central Electricity Research Laboratories (CERL) of the former Central Electricity Generating Board (CEGB) at Leatherhead, Surrey, England. Barry Dooley is the author or coauthor of over 260 papers and the editor of 14 international conference proceedings, primarily in the areas of metallurgy, power generation, boiler tube failures, HRSG tube failures, cycle chemistry, and life extension and assessment of fossil plants. He is the coauthor of a three-volume book on boiler tube failures, a two-volume book on steam turbine damage mechanisms, and a book on flow-accelerated corrosion in power plants. Barry Dooley is the executive secretary of the International Association for the Properties of Water and Steam (IAPWS). He was awarded an Honorary D.Sc. from the Moscow Power Institute in 2002.

Michael Rziha was working from 1983 until January 2019 at Siemens Power Generation. He had initially started in the chemical analytical laboratory in Erlangen before he became a Chemical Commissioning Engineer, where he was involved in numerous projects (nuclear and fossil fired and combined cycles) around the globe during their commissioning period until 1995.

From 1995 on he worked for 3 years in the Design Department of Siemens Power Generation for Water Treatment Plants and Power Plant Chemistry. Between 1998 and 2013 he was the head of Department Power Plant Chemistry and Chemical Cleaning. Part of his duties included leading the Department for Plant Cleaning Concepts as well as the Chemical Commissioning Engineers, who are responsible for the entire chemistry of a power plant during erection and commissioning for 15 years. Beside that he also supported over many years the O&M group in all matters related to operational chemistry questions. In 2013 he was appointed as Key Principal Expert for Plant Chemistry at Siemens PG.

Since February 2019 he started at PPCHEM AG, Hinwil, Switzerland as Chief Key Expert for Plant Chemistry to conduct worldwide Seminars, Lectures and Conferences on all power plant chemistry related topics, as well as to provide individual technical consultancy.

Paul McCann (M.S., Chemistry, University of Nottingham, UK) is a specialist in power plant steam/water cycle chemistry, corrosion and water treatment at the E.ON Technologies Ltd. global unit in the UK. He has over 15 years' experience in the power industry, joining Powergen, subsequently E.ON, in 1999. Paul is also the current chair of the British and Irish Association for the Properties of Water and Steam and the vice-chair of the Power Cycle Chemistry Working Group of the International Association for the Properties of Water and Steam.

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