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**White Paper (pre-TGD)
Corrosion Product Sampling, Monitoring and Analysis for Flexible and Fast
Starting Plants**

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Summary

This White Paper considers the sampling and monitoring of total iron and copper corrosion products for flexible and fast starting conventional and combined cycle/HRSG plants. It also provides the necessary guidance for operators to determine if the operational and shutdown cycle chemistry are optimum or need improvement. A new systematic approach for evaluation of corrosion product transport during startup is introduced. This method is a key measure in optimizing the shutdown chemistry and preservation measures. Guiding values covering various combinations of plant types, metallurgies, feedwater chemistries are summarized in the IAPWS Corrosion Product Decay Map allowing a simple and direct grade of the results of the measurement during startup, and suggestions for improvement.

This Technical Guidance Document contains 52 pages, including this cover page.

Further information about this Technical Guidance Document and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS (Dr. R.B. Dooley, bdooley@iapws.org) or from <http://www.iapws.org>.

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1. Nomenclature and Definitions (extracted from TGD6-13.

Needs to be brought up to latest version in FFS TGD

Term	Alternative or Acronym	Definition
All-volatile Treatment	AVT	Conditioning regime in which only volatile alkalizing agents are added to the feedwater (commonly ammonia, but other volatile amines may also be employed)
	AVT(R)	May be either:
	AVT(O)	Reducing conditions (added reducing agent) or Oxidizing conditions (without reducing agent)
Air-cooled Condenser	ACC	System to condense steam from a turbine by indirect air cooling
Condensate		Water that derives from condensation of steam after expansion in a steam turbine and passage through a condenser or process heat exchanger. “Main condensate” refers to the condensate from the turbine condenser including its possible tributaries up to the end of LP feedwater heaters
Conductivity	Specific Conductivity	Electrical conductivity of the water sample as measured directly without any treatment
	Direct Conductivity	
Conductivity after cation exchange	CACE	Conductivity of a water sample after passage through a strongly acidic cation exchanger in the hydrogen form
	Cation Conductivity	
	Acid Conductivity	
Caustic Treatment	CT Hydroxide Dosing	Involves addition of NaOH to the boiler or HRSG evaporator
Drum boiler		Boiler in which steam (generated in heated evaporator tubes) is separated from water in an unheated horizontal pressure vessel (drum). The liquid phase is recirculated to the evaporator.
Feedwater		Water that is being pumped into a boiler or HRSG to balance the steam production; usually understood as water passing from the deaerator and/or the high-pressure heaters to the boiler

Term	Alternative or Acronym	Definition
Flow-accelerated Corrosion	FAC	Accelerated corrosion of carbon steel components in the feedwater system and HRSG evaporators caused by chemical dissolution of magnetite on the surface and exacerbated by turbulence in the flow
Heat Recovery Steam Generator	HRSG	Plant that generates steam using heat transfer from the exhaust gas of a combustion (gas) turbine
Once-through boiler or HRSG		Boiler in which output steam is generated from input water by complete evaporation. There is no recirculation of boiler water.
Oxygenated Treatment	OT	Conditioning regime in which ammonia and oxygen are added to the feedwater
ppb, ppm	$\mu\text{g/kg}$, mg/kg	Fraction of the quantity of a substance in another substance (quantity per quantity). In power cycle chemistry commonly used for describing the mass fraction (mass per mass) of a substance in steam or water. Its use as “concentration” (quantity per volume) is ambiguous and formally incorrect.
Phosphate Treatment	PT	Conditioning regime for drum boilers in which alkalinity is achieved by dosing tri-sodium phosphate to the boiler water

2. Introduction: Purpose of Document and How to Use It

This White Paper (preliminary TGD) is an extension of the 2013 IAPWS Technical Guidance Document for Corrosion Product Sampling and Analysis [1] (TGD6-13) that has been widely accepted. This extension widens the application area from steady-state conditions to variable conditions. Consequently, the purpose of these analyses is widened from monitoring the effect of feedwater chemistry to cover other processes, especially preservation during shutdown, that contribute to the level and transport of oxides in the condensate and feedwater systems.

Provided correct sampling conditions and appropriate sample splitting for on-line instruments, proxy methods such as turbidity, particle counting, and determination of particle size distribution give robust and reliable data for level and transport of particulate matter related to iron and copper corrosion products as well as oxides stemming from steam circuits. This TGD explains how to use the proxy-methods correctly to track metal oxides during steady and transient load, and even during startup. To relate the output of the proxy methods to the classical analytical values, a method for filtered iron is introduced that correlates with the particle-based on-line methods. The on-line methods may be used to minimize further the transport of corrosion products and other oxides to the evaporator where they deposit and adversely affect the thickness of the oxide layer on the tubes, which in turn has negative effects on heat transfer, under-deposit corrosion, and time between chemical cleanings. Most importantly, they may be used to track and quantify the corrosion products transported to the boiler during startup. The White Paper introduces a procedure for quantification of this key parameter that reflects the success or failure of the preservation measures applied during shutdown. Based on thorough international experience, the IAPWS Corrosion Product Decay Map grades the outcome of this measurement during startup in a simple and illustrative manner. This allows the operator to plot the local results directly against the international experience and to improve the operational and shutdown chemistry in a move towards more optimal conditions in the future.

IAPWS has recently issued a series of Technical Guidance Documents for the cycle chemistry control of conventional and combined cycle plants [2,3,4,5]. These documents can be applied to co-generation plants as well as those conventional and combined cycle plants. The volatile treatment and phosphate/caustic documents include suggestions for the levels of corrosion products at key locations around the plant cycle for steady state operation. When a particular plant has the cycle chemistry optimized, the general corrosion and flow-accelerated corrosion (FAC) in the feedwater, condensate, and low temperature circuits where attack can be the highest should be minimal. Otherwise, components such as feedwater and condensate piping, and tubing in the low pressure circuits of HRSGs, can become thin and ultimately fail. The corrosion produces iron oxides in all plants and copper oxides in plants with mixed-metallurgy materials, the latter most often including copper-based alloys in feedwater heater tubing. The corrosion products consist of both dissolved and particulate oxides, which are transported throughout the water-steam cycle and deposit on higher pressure heat transfer surfaces. These deposits can impede heat transfer, affect the performance of the boiler, HRSG or steam turbine, and most importantly they can act as initiating

centers for other failure/damage mechanisms such as under-deposit corrosion (UDC) on boiler waterwalls and HRSG evaporator tubing. This mechanism is well understood and described in recent literature [6,7,8].

For plants with frequent start/stops, the chemical conditions during shutdown/layup significantly influence the transport of corrosion products during operation. This means that for this kind of plants, e.g. operating two-shift with daily start/stop, consideration of the shutdown chemistry is as important as the feedwater chemistry during operation in minimizing the transport of corrosion products and the adverse effects of it. For many years it has been well understood that the corrosion product levels are well elevated during startup periods above the IAPWS levels for steady-state operation [1], and that often these periods can extend to many hours. As a result, the corrosion product levels in some plants may never reach or decay to the steady-state IAPWS levels, unless the shutdown chemistry is optimized to produce lowest possible corrosion products.

It should be noted that the feedwater and boiler/evaporator treatments for the conventional and combined cycle/HRSG plants have been published in previous IAPWS Technical Guidance Documents [4,5]. The Normal/Target values promulgated in these documents and customized as needed, consistent with the plant characteristics, are expected to produce the minimum levels of corrosion products and thus these values remain the same.

The existing TGD6-13 [1] on corrosion product sampling and analysis is designed to supplement the IAPWS documents on cycle chemistry to ensure that corrosion products are monitored using adequate and effective sampling and analytical techniques under steady state conditions. It can be used directly by chemists and plant operators and will be useful for the development of guidelines at the international, national, company and manufacturer level. It can also be used in the design phases of generating facilities to ensure that the optimum sampling locations are provided and that there is appropriate analytical equipment for the chemistry laboratory and/or steam/water sampling systems (sometimes called wet racks).

The primary purposes of that document in conventional and combined cycle/HRSG plants is to:

- a) highlight the problems that can exist with the physical sampling of corrosion products in flowing water and steam,
- b) indicate how these problems occur and can be avoided,
- c) indicate the key plant locations where sampling should be conducted,
- d) provide an outline of an optimum sampling system for the representative sampling of corrosion products,
- e) highlight the various analytical methods that can be used for the analysis of corrosion products with the advantages and disadvantages of each method clearly outlined,
- f) suggest a level of quality control to ensure reliable analysis.

It is emphasized that the existing TGD6-13 [1] is an IAPWS Technical Guidance Document representing the cumulative experience of IAPWS PCC Working Group members worldwide. It provides guidance on the best practices for sampling and analyzing corrosion products in conventional and combined cycle/HRSG plants **under steady-state conditions** to indicate that the chemistry treatments and operating regimes customized for a plant are optimal, that general corrosion and FAC are minimized, and to determine if the operational cycle chemistry are optimum

or need improvement. Performing these tasks properly provides the operator/chemist some assurance that the plant is not likely to fail and is safe for the plant personnel.

The present White Paper (pre-TGD) extends the methodology for sampling and measurement of corrosion products (and other particulate oxides) to transient load conditions and even the very variable conditions under startup. This calls for on-line measurements by means of proxy methods (such as turbidity and particle counting) to handle the quickly varying levels of oxides during load transients and startup. But the outcome of the proxy methods must have a high correlation with the classical analytical measurement of corrosion products to relate to existing guiding values under steady-state and to establish new guidance for the transient situations. The filtered iron [⁹] (or copper) method introduced in this document constitutes the link between the particle-based proxy methods and the reference methods. Experience [¹⁰] gained during the research phase of this White Paper (pre-TGD) indicates that the filtered iron results correlate well with the responses of the proxy methods.

The most important application of the methods introduced here is the quantification of the iron and or copper oxides transported to the boiler or HRSG evaporator during startup. This White Paper (pre-TGD) introduces an approach to measure this and to relate it to the international experience condensed in the IAPWS Corrosion Product Decay Map. This map graduates the key figures of a startup, i.e. the amount of corrosion products transported and the time necessary to reach the level of corrosion products comparable with the guiding value for steady operation, on a scale from optimum to poor operational and shutdown chemistry. From the illustrative comparison with operational experience and the marked effect on the startup time, operators will naturally seek to improve operational, preservation and shutdown chemistry to perform better in the future.

During the research for this White Paper (pre-TGD), it has empirically been observed that the distribution of corrosion product results follows the log-normal distribution¹¹, and that this relates to the particle size distribution of the oxides in the samples. Recognition of this leads to some practical consequences:

- The occasional elevated results observed in a series of CP analyses over shorter or longer times are not random outliers and should be treated as a part of the data set.
- The level and variability of CPs using aggregated values should be reported as median values and 95th percentile^a instead of average and standard deviation as those assume a normal distribution behind the data.
- The median value and 95th percentile are readily calculated in any spreadsheet or statistical program, and they are easy to communicate and well suited as guiding lines in graphical displays as trend curves.

The appendix (Section 10) describes further the treatment and reporting of data according to the log-normal distribution. The aggregation of data into median and percentile values should be used in general for CP results, no matter if they are acquired under steady-state or flexible conditions.

Both guidance documents can form the basis of, but should not restrict, other derivative guidelines around the world. Experience has indicated that, depending on local requirements, the processes

^a The 95th percentile is the value (concentration of CP) that 95 % of the measured results are less than.

and procedures described will provide good reliability and availability if they are customized for each plant depending on the actual conditions of operation, the equipment installed, the materials used in different parts of the cycle, and the condenser cooling media.

It is further emphasized that the guidance values given should not be considered as manufacturer's guarantees. Adoption of the optimum sampling and analytical processes described in the TGDs may provide levels of iron and copper corrosion products that are different from those suggested by manufacturers. Each manufacturer should provide a set of target values representing the plant as designed, and these may be slightly different from the operating guidance provided in the original document.

3. The Challenge of Flexible Plant Operation and Corrosion Product Sampling and Analysis

The current IAPWS Technical Guidance Document [1] provides definitions, technical descriptions and guidance for corrosion product sampling (CPS) for steady state/base load operation plants only. The IAPWS TGD development team has been tasked with the identification of issues and knowledge gaps related to the CPS and CPT&D for flexible operating plants.

This White Paper (pre-TGD) outlines the problems, influences, state of knowledge and knowledge gaps related to CPS for flexible operating plants.

Finally, proposals are suggested for solutions to these issues as well as suggesting directions for guidance and customization of that guidance.

3.1 Statement of Problem:

The purpose of this White Paper (pre-TGD) is to provide information on how to representatively sample, analyze and interpret CPS results for flexible operation plants so that the correct cycle chemistry related actions can be taken to minimize corrosion, corrosion product transport & deposition, and the risk of plant failures.

For plants operated according to the IAPWS guidelines on feedwater and boiler water chemistry [4,5] the corrosion during steady-state operation will be minimized. However, many plants worldwide operate in the flexible manner with frequent load changes, several start/stop events per month or even daily start/stop. Preservation during these short stops can be an issue: the optimum preservation measures are often compromised to meet the unpredictable generation dispatch, and this certainly affects the shutdown chemistry and can allow corrosion during shutdown that increases the transportation and deposition of corrosion products in the next startup. For this kind of plant, the major contribution of corrosion products carried to and deposited in the boiler or evaporator - with adverse effects on heat transfer, under-deposit corrosion, and periods between acid cleaning - may be associated with startups and the many load changes during operation. Most of the transported corrosion products may be caused by the chemical conditions under shutdown that do not properly suppress corrosion. Thus, there is a need for methods to track the corrosion products under such quickly varying conditions as load changes and startup. Such measurements should be used to minimize corrosion product transport in operation and specially to improve the shutdown chemistry. Optimized preservation will have a tremendous effect on the corrosion

product transport and improve several operational quality parameters, not least the time used during startup to reach corrosion product levels corresponding to the guiding values for normal operation.

For plants with superheaters tubed in high alloyed steel, e.g. austenitic materials, exfoliation of steam magnetite during the cooling and heating phases associated with an outage may depending on the shutdown period contribute considerably to or even dominate the iron oxides transported in the condensate and feedwater trains during operation. The production of these oxides is not influenced by feedwater chemistry or preservation measures, but solely determined by the oxide thickness and the temperature transients of the material during the cooling and heating phases¹². Measurement of this kind of oxide may help identify the events when loosely deposited particles are brought in suspension and thus transported towards the boiler. This knowledge is the first step in identifying operational means to minimize the oxide transport to the boiler. Measurement during startup may in this case help optimize the startup procedure, e.g. by introducing or improving steam blowing of the superheaters during the initial phases. Exfoliated oxides removed in this way will not be observed in the condensate during later phases of the startup.

The intention is for the present White Paper (pre-TGD) to provide robust, scientifically accurate and practical guidance to provide resolution to this statement of problem

3.2 Background to Dissolved and Total Corrosion Products

Corrosion products can circulate in the water-steam cycle in dissolved and particulate states.

Dissolved Corrosion Products means that the corrosion product (iron, copper, etc.) is present in ionic form or as simple (e.g., monomeric, dimeric) hydrated species in the sample at the time of sample collection.

The aqueous corrosion of a metal immediately forms positive metal ions (cations) at its surface. This is an oxidation (anodic, in electrochemical terms) process involving the release of electrons that react with the oxidant close by on the surface. The oxidant will be just the water in a deaerated environment or dissolved oxygen in an aerated environment, and its reaction with electrons is the balancing reduction (cathodic, in electrochemical terms) process that typically forms negative ions (anions) such as hydroxide. The cations combine with the anions and form a corrosion product layer of oxide on the surface while some stay in solution and are transported to the bulk fluid. There, they may stay in solution or some may precipitate as particles of oxide in suspension. Also, depending on the chemical and physical condition of the fluid (pH, temperature, flow rate), the oxide film itself may tend to dissolve or release particles by erosion. The overall process is clearly dependent on the oxidation-reduction potential (ORP) of the fluid. ***Particulate Corrosion Products*** are suspended particulate solids (usually oxides or hydroxides) at the time of sample collection. They might precipitate directly in the fluid phase or be released from the layer on the metal surface in water-touched components, or during an electrolytic (galvanic) corrosion process as end products of the electrochemical reaction.

The relationship between Dissolved, Particulate and Total Corrosion Products is given in the following equation:

$$\text{Total Corrosion Products} = \text{Dissolved Corrosion Products} + \text{Particulate Corrosion Products}$$

In all cases the corrosion products originate from corrosion processes and either type can transform into the other, depending on the chemical and physical conditions at the various locations in the water-steam cycle. For example, the solubility of iron ions in flowing water in a temperature range of 50–300 °C is strongly influenced by pH and temperature, so precipitation and dissolution can occur around a circuit.

Such transformations often take place at locations in the water-steam cycle where the conditions change continuously or drastically. This is the case for example in the turbine during steam expansion. Temperature and pressures drop steadily with the result that the steam becomes oversaturated for example in copper. Copper (oxide/hydroxide) precipitation follows on the high pressure (HP) turbine blades, which can result in reduced efficiency, increased axial thrust, increased vibrations, etc.

Similar phenomena can be observed for iron cations in the condensate level-control valves of the HP and LP pre-heaters, where the pressure is reduced drastically. Therefore, the condensate at boiling point partly evaporates (flash-effect). This adiabatic expansion leads to a drop in temperature of the remaining condensate. Oversaturation of the condensate in iron cations might be the result, followed by precipitation of magnetite (Fe_3O_4) in the valve body or cage that finally leads to malfunction of the valve.

It is good practice to analyze, monitor, and try to minimize the amount of dissolved and particulate corrosion products in the condensate, feedwater, and boiler/evaporator water at various locations in conventional and combined-cycle/HRSG power plants. Note that assessing particulate concentrations involves sample filtration, so the practical definition of particles in terms of their size depends on the pore size of the filter medium. Common definitions for power plant cycles are 0.45 μm and 0.20 μm . It follows that “dissolved” corrosion products involve all those that pass through the filter, even though they will contain very small particles.

3.3 Corrosion Product Sampling, Rationale and Sample Locations

The results from sampling and analysis of corrosion products in conventional and combined cycle/HRSG plants provide the fundamental indicator of whether there is an effective cycle chemistry program in place for any steam raising plant while it is at a referenced operating condition which is the same for each sampling period; e.g., steady operation at full load. The same processes should be used to assess any changes to the chemistry treatments or to operating guideline values in efforts to optimize the plant cycle chemistry.

To provide an indication of the levels of corrosion products in some of the main conventional and combined cycle/HRSG plants, the following points are delineated to provide some guidance in the other sections of this document. **Note that the values provided are for steady-state, full load, operation only and not for any transient conditions.**

- Conventional plants with all-ferrous feedwater systems. Monitoring corrosion products at the economizer inlet provides an indicator of whether the feedwater treatment is appropriate and whether there is any FAC occurring. As covered in the IAPWS treatment TGDs [4,5], the level of total iron at this location is dependent on the feedwater treatment. Levels below 1 $\mu\text{g}/\text{kg}$ for units on oxygenated treatment and below 2 $\mu\text{g}/\text{kg}$ for units on AVT are typically easily achievable with optimized cycle chemistry.

- Conventional plants with mixed-metallurgy feedwater systems. Monitoring corrosion products at the economizer inlet provides an indicator of whether the feedwater treatment is appropriate, whether there is any FAC occurring, and whether the copper alloys in the feedwater heaters are protected. As covered in the IAPWS treatment TGDs [4,5], the levels of iron and copper at this location are dependent on the feedwater treatment. Levels of total iron and copper below 2 µg/kg for units on AVT are typically easily achievable with optimized cycle chemistry.
- Conventional plants with all-ferrous and conventional plants with mixed-metallurgy feedwater systems. As indicated in the IAPWS TGD for volatile treatment [4], monitoring the cascading drain lines provides an indicator of whether two-phase (steam-water) FAC is controlled. It is most effective in these situations to monitor the drain from the lowest high pressure (HP) heater. Levels of total iron (dissolved and particulate) below 10 µg/kg are typical for optimized cycle chemistry with feedwater pHs around 9.8.
- Combined cycle/HRSG plants. Monitoring corrosion products in the feedwater and evaporator drums provides an indication of whether single- and two-phase FAC are controlled in the preheater (low pressure (LP) economizer), LP evaporator, LP risers and drum components, IP and HP economizer, IP evaporator, and IP evaporator and risers. Often for HRSGs it is sensible to monitor total iron at the inlet and outlet of the preheater and LP economizer circuits. As covered in the IAPWS treatment TGDs [4,5], the level of total iron at these locations is dependent on the feedwater and condensate treatments. Levels of total iron less than 2 µg/kg in the feedwater and less than 5 µg/kg in each drum are typically easily achievable with optimized cycle chemistry.
- Conventional plants and combined cycle/HRSG plants in general. Monitoring steam for total iron levels provides no indication of the condition of the cycle chemistry control and is ineffective as a means of drum carryover detection. Monitoring steam for copper in units with mixed-metallurgy systems is dependent on the drum pressure and the solubilities of the cuprous and cupric hydroxides. As suggested in the IAPWS TGD on Steam Purity [13], the copper level in steam is dependent directly on the feedwater chemistry, and once this is optimized and the copper levels at the economizer inlet are around 2 µg/kg then copper levels in saturated steam and main steam should consistently also be less than 2 µg/kg. Note that there are no target values in the IAPWS TGDs for either Fe or Cu in steam.
- Conventional and combined cycle /HRSG plants with air-cooled condensers (ACC). Monitoring corrosion products in the condensate before and after a condensate filter provides an indicator of whether corrosion and FAC are minimized in the ACC at the tube entries in the upper transport ducts (streets). As covered in the IAPWS volatile treatment TGD [4], the level of total iron (dissolved and particulate) at these locations is directly dependent on the feedwater/condensate pH. Levels of total iron below 10 µg/kg are consistently achievable with pH levels around 9.8. Downstream of a typical filter (5 µm absolute) the levels can be consistently controlled to around 5 µg/kg.

- Cogeneration plants with condensate return systems. For a cogeneration plant that sends steam to a steam host for use in a process (either via direct or indirect use) and then receives all or a portion of the condensate back, monitoring corrosion products in the return condensate indicates whether corrosion and FAC are minimized in the process part of the steam host plant. High corrosion product levels in return condensate in cogeneration plants are not uncommon. It is common for condensate filters to be utilized in cogeneration plants prior to the condensate being returned to the boiler or HRSG system. Levels of total iron below 10 µg/kg are consistently achievable with pH levels around 9.8 for all-ferrous plants. As indicated above, downstream of a filter (5 µm absolute) the levels can be consistently found to be around 5 µg/kg. For mixed-metallurgy plants the copper levels can be extremely variable depending on the plant design and operation, but with the chemistry optimized as far as possible levels of total copper less than 10 µg/kg can be expected.

Table 1 gives an overview of the sample points mentioned above for classical corrosion product monitoring.

Table 1: Summary of key corrosion product sampling locations

Type of Plant	Sampling Locations								
	ACC Outlet*	Condensate Filter Outlet*	Condensate Pump Discharge	Process Condensate Return	LP & HP Heater Drains	Deaerator Inlet	Economizer Inlet	Boiler /Evaporator	Saturated or Superheated Steam
Conventional – All Ferrous	X	X	X		X		X		N/A
Conventional – Mixed Metallurgy	X	X	X		X	X	X		N/A
Combined Cycle/HRSG Plants	X	X	X				X	X	N/A
Cogeneration Plants	X	X	X	X			X	X	N/A

* If ACC or condensate filters installed

With the procedures introduced in this White Paper (pre-TGD) there are **two basically different rationales behind corrosion product analyses**: The classical procedure takes samples under well defined, steady, high load conditions to be able to compare results between campaigns and with the IAPWS guidance given above. The purpose of that is to optimize and customize the feedwater chemistry of the plant, follow up on this by an occasional routine check of status quo, or to document the effects of changes in the chemistry program. Guidance covering this purpose is given in the first corrosion product sampling and analysis TGD6-13 [1]. The procedures and methods outlined in this document focus on the measurement of corrosion products and other oxides during transient load and startup situations, i.e. the opposite of steady-state operation. The purpose of such measurements is to characterize the transportation of corrosion products (and other oxides) to the boiler as a means to minimize it by changes in procedures for e.g. operation, preservation and startup, so that less particles are carried into the condensate and feedwater systems. Such actions are not directly related to the feedwater chemistry but may often be responsible for the major part

of the corrosion products or other oxides eventually transported to the boiler through the feedwater system.

4. Sampling – Sample Conditioning and Sampling Procedures

The governing principles and practical realization of sampling systems are covered in detail in TGD6-13 [1] and are not repeated here. Instead the conclusions are summarized and commented with respect to the application in focus of this TGD.

4.1 Summary of Optimal Aspects of Sample Conditioning

Table 2 states the basic components and considerations to obtain representative CP samples.

Table 2: Summary of optimal sample conditioning system aspects for corrosion product sampling

System Aspect		Description	Comment
1	Sample Nozzle	Non-isokinetic sample nozzle required for sampling water	Optimal location is in a straight section of pipe, 40 pipe diameters downstream of any flow disturbances
2	Sample line	Type 316L stainless steel tubing, Reynolds number for straight runs > 2300 to ensure turbulence and to avoid particle deposition	Sample line run needs to be continuously sloped and as short as practical. Line sizing needs to take pressure drop into account while ensuring turbulent flow
3	Sample line bends	Sample line bends to be gentle with a minimum bending radius of 60 mm to ensure turbulence and to avoid particle deposition	Expansion loops should be in the horizontal plane and as few as possible
4	Sample isolation valves	Should be constructed of 316L stainless steel	Isolation valves should be fully open when system is in service
5	Sample cooler	Correctly sized for heat transfer with the largest coil diameter possible. Critical Reynolds number for bends to ensure turbulent flow and to avoid particle deposition needs to be determined for each design	It is important to ensure turbulent flow in sample cooler. The relationship between tubing diameter and coil diameter and its impact on Reynolds number must be understood
6	Sample line liquid velocity	> 1.9 m/s for typical systems with 4 mm internal-diameter lines and 50 mm-diameter cooling coil when sampling for corrosion products. To be sustained for at least 2 hours prior to sample collection	During periods when no corrosion product sampling is occurring, lower sample line velocities are acceptable.
7	Sample line filters	Any sample line filters should be removed or bypassed prior to sampling for corrosion products	
8	Sample pressure reduction valves	Valves need to be resistant to blockage and erosion	Needle valves unsuitable for high pressure applications (> 30 bars)

The length of the sampling line influences lag times and especially the time needed to flush the line down. **Short sampling lines, optimally placed locally in the plant at the most important sampling points, are thus preferable. This statement is particularly noteworthy when CP levels are monitored during startup and transient load situations, i.e. when quickly varying levels are to be expected.**

4.2 Optimal "Grab" Sampling of Iron and Copper Corrosion Products

Chemical analysis of grab samples continues to be the reference method for monitoring CP levels and transport for plants operating in the flexible mode. Even when proxy methods are applied for on-line monitoring, the results must be correlated with results of grab samples to interpret them correctly. Table 3 is based on the corresponding table in TGD6-13 [1] but modified to cover situations with flexible operation.

Table 3: Optimal Grab Sample Methodology for Corrosion Products

Number	Optimal Grab Sampling Action	Comment
1	Obtain high density polyethylene (HDPE) bottles	HDPE is preferred but other materials may be used if suitable for use with ultra-low concentrations of metals. Bottles for corrosion product sampling are best used only once and then discarded unless they can be thoroughly cleaned and returned to an uncontaminated state. NOTE: For samples intended for later filtration, 1 L volume is recommended.
2	Clean bottles and caps thoroughly prior to use with ultrapure water	Water should be high purity with ultra-low concentrations of metals
3	Add high purity concentrated nitric acid to bottles – 0.5 mL of concentrated nitric acid for each 100 mL of bottle volume	Nitric acid minimizes the deposition of corrosion products onto the internal surfaces of the bottle. NOTE: Do not add acid to bottles for filtration samples as this will partly dissolve particles.
4	If sampling for total corrosion products, ensure no filters or strainers are present in the sample line	If particulate levels of corrosion products are to be determined, appropriate filtration should be done separately
5	Open sample line valve and establish sufficient sample flow to ensure turbulent flow at the given (low at startup) pressure	Continuous sample flow is preferred. NOTE: For sampling during startup, sample lines should be opened as soon as condensate and feedwater pumps are in operation and enough flow can be realized.
6	Leave the sample line untouched during the sampling period, only adjust flow if absolutely necessary due to increasing pressure	This is to establish a steady-state condition of the whole sample system. NOTE: For monitoring during transient operation, continuous sample flow should be maintained during the complete campaign/extended sampling period.
7	Begin sampling in relation to the expected event: Prior to a load change or at First Fire during startup	NOTE: During startup or transient load, the feedwater and/or condensate flow should be recorded for each sample. In practice, record the exact sampling time and read the load from the relevant trend curves in the DCS.

Number	Optimal Grab Sampling Action	Comment
8	Without flushing, fill the sample bottle completely and seal with lid	Flushing with the sample fluid will result in the loss of the nitric acid preservative. NOTE: Samples for filtration may be taken in 1 L sample bottles and filtrated afterwards. Alternatively, the filtration may be done on-site by use of filter holder with a membrane filter attached directly to the sample outlet. In that case, measure the filtrated volume by means of a 1 L cylinder glass.
9	Send sample bottle to laboratory for digestion and analysis	Samples should be analysed without delay to minimize the risk of corrosion products attaching to sample bottle internal surfaces. NOTE: When relevant, samples should be filtrated as soon as possible after sampling.
10	After sample analysis, sample bottles should be discarded if they cannot be thoroughly cleaned	Sample bottles should not be re-used for future corrosion-product sampling unless they can be returned to their pristine state



As mentioned in Table 3, samples for filtered iron may be filtrated in the laboratory shortly after sampling by means of standard laboratory equipment and suction, or on-site using a filter holder attached directly to the sample point. The last method is handy especially when chemical analysis is not done at a laboratory nearby. In that case, the filters may be dried in a protected place (no dust), packed in a suitable case that maintains the filter surface intact, and transported or sent to the laboratory. Figure 1 shows the two setups for filtration through membrane filters.

Figure 1. Filtration of filtered iron samples on-site or after sampling in the laboratory. The filter holder may be connected to the sample point by a flexible tube and a clamp.

4.3 Optimal Sampling for On-Line Proxy Methods

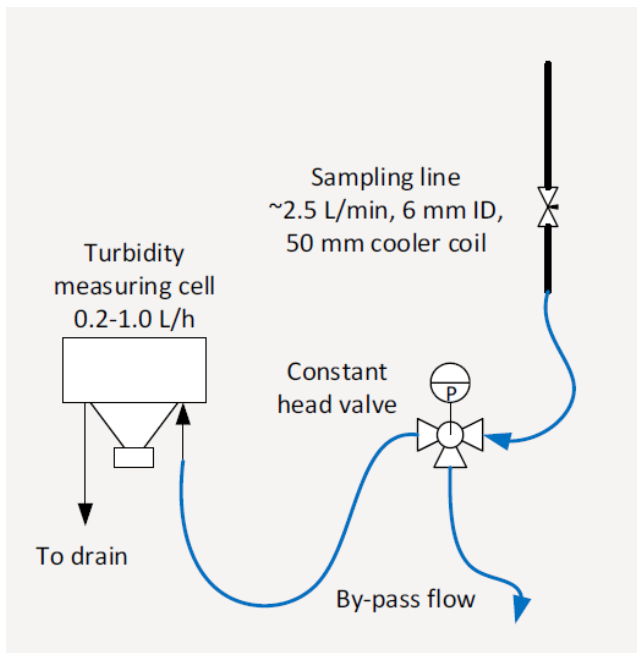


Figure 2. Combining the high turbulent flow rate with the lower, steady flow rate for e.g. a turbidity measurement.

The demands for turbulent sample flow to obtain representative CP samples are contradictory to the specification of the proxy methods for a steady, low flow to the measuring cell. Where the turbulent flow conditions call for flow rate of typically 2-3 L/min, most proxy method instruments demand steady flow rates less than 1 L/min and often in the range 0.05-0.5 L/min. The contradiction is elegantly solved by means of a constant head device or back-pressure relief valve. Both are valves that split the sample flow into a sample stream to the instrument and a bypass stream to drain. The valves maintain a constant, adjustable pressure on the instrument outlet, and thus the optimal steady flow for the monitor may easily be tuned in. When the pressure in the sample line varies due to e.g. load variation, the valves divert more or less of the main

sample stream to the by-pass maintaining the steady flow to the instrument. Figure 2 illustrates the connection of a proxy instrument to a sample point.

The use of a constant head device is critical for obtaining interpretable data from proxy methods. If not used, the sampling conditions will be far from those necessary to get a representative sample, because the flow rate must be reduced to meet the demands of the instrument. Furthermore, the proxy response will be affected by the unavoidable flow variation of the sample line. Experience shows that the proxy response under such faulty conditions is only vaguely related to CP levels and operating conditions of the plant.

5. Corrosion Product Analytical Methods

5.1 Analytical Methods – Particulate Digestion

Analytical methods for iron corrosion products are described in Table 4. The commonly applied spectrophotometric analytical methods require the iron to be in the ferrous (Fe(II)) state. This requirement necessitates the samples to be acidified and any particles and sampler filters or membranes to be fully dissolved prior to analysis.

A number of different digestion methods are available, with the most common being boiling nitric acid digestion [14] and 2-sulfanylacetic acid (commonly known as thioglycolic acid) digestion at 90 °C. Thioglycolic acid digestion is recommended for use with the disodium-4-[3-pyridin-2-yl-6-(4-sulfonatophenyl)-1,2,4-triazin-5-yl]benzenesulfonate analysis method (commonly known as the Ferrozine analysis method) for iron. Regardless of the digestion method, it is critical that after digestion there are no particles remaining in the sample and that all the iron and copper are fully dissolved. The digestion process can lead to loss of liquid, in which case only high purity demineralized water should be used for volume replacement.

When using grab samples for total corrosion products, the sample should not be filtered either before or after the digestion step, since this will remove particulate species and result in a non-representative, low result. As indicated above, filters and membranes from laboratory or on-site filtration and integrating samplers must be fully digested as well. Comparison of filters with the Babcock & Wilcox Membrane Filtration Charts mentioned in Table 4 is a convenient way to get an estimate of the content of iron in the sample and to decide, if extra thioglycolic acid (double or quadruple of the standard amount) should be added before digestion.

5.2 Overview of Analytical Methods

Table 4 gives an overview of common methods for CP analysis. The table is essentially like the corresponding table in TGD6-13 [1] except for the description of the method for filtered iron. This method [9] consists of dissolving the CPs deposited on a 0.45 µm filter by filtration of a 1 L sample by digesting it in diluted acid (e.g. the standard volume of nitric or thioglycolic acid for grab samples diluted to 50 mL with ultrapure water). Afterwards the dissolved iron is analysed by any of the standard analytical methods mentioned in Table 4. Due to the concentration factor (20) by accumulating the CPs from a 1 L sample into a 50 mL final sample volume, the detection limit of the method is comparable to that of the advanced ICP-MS technique. The low detection limit may be achieved by means of common and relatively low cost methods such as the Ferrozine method. The filtered iron result does not express the total iron content of the sample,

because particles less than 0.45 µm and dissolved iron species pass the filter. Under oxygenated treatment (OT) conditions 70-90 % of the total iron is expected to be retained on the filter. If not then this is an indication of ongoing corrosion taking place upstream of the sampling point. As this method concentrates on particles in the sample, the correlation with the particle-based proxy methods is better than that observed for total iron methods.

The Babcock & Wilcox Membrane Filtration method, in which the iron content is estimated by comparison with a set of reference charts, is not particularly sensitive or precise. However, it is adequate for use in situations when iron concentrations higher than 10 µg/kg are expected and several samples must be taken in sequence. Due to the simple quantification, it is suited for tracking the iron levels during a startup or under transient load conditions. It gives a rough estimate of the iron content only, but this may be sufficient to track such situations with large variation in content over time. Higher precision may be obtained afterwards by digestion of the filters and subsequent analysis as described above. In that sense, it may be considered a "poor man's proxy method" and used correspondingly, if an on-line measurement is not available at the given plant.

Table 4: Summary of Analytical Methods for Iron

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Babcock & Wilcox Membrane Filter Comparison Charts ¹⁵	Collection of liquid-only sample then filtering a known volume through a 0.45 µm filter under vacuum ¹⁹	Particulate iron only. Five filter charts available for: 1. Magnetite Fe ₃ O ₄ only 2. Hematite Fe ₂ O ₃ .xH ₂ O 3. 2:1 Hematite: Magnetite ratio 4. 1:1 Hematite: Magnetite ratio 5: 1.5:1 Hematite: Magnetite ratio	1-L sample, cooled after pressure reduction but before sample line filters	Method is a visual comparison to a commercially available reference chart developed originally for the commissioning of once-through boilers. Separate charts available for reducing and oxidizing environments and various ratios of hematite and magnetite. Approximate detection limit is 10 µg/kg. Comparison-chart increments are 10, 25, 50, 75, 100, 250, 500, and 1000 µg/kg.	Method is only suitable for the indication of particulate iron, primarily during startup, transient load conditions, and new power plant commissioning. Should not be used for steady-state corrosion product analysis due to the high detection limit. Method is suited for tracking iron levels during startup and transient conditions when easy quantification counts more than high precision. The method may be used as a simple proxy technique.

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
				Thus, the technique provides a gross overview.	
Filtered iron [9]	<p>Collection of 1 L liquid-only sample, then filtering through a 0.45 µm filter under vacuum. Alternatively, filtration of 1 L on-site by means of a filter holder and a push-fit connection to the sampling point outlet.</p> <p>Filters are then digested to 50 mL final volume. Total iron determined via suitable dissolved iron analysis method such as ICP-MS, UV-Vis Ferrozine method or AA. Measured total iron concentration is divided by 20 to give the filtered iron concentration in the original sample.</p>	Particulate iron only, i.e. filtered Fe	1-L sample, cooled after pressure reduction but before sample line filters	<0.3 µg/kg, as per iron analysis method selected	<p>Preferred method for correlation with instrumental, particle-based proxy methods.</p> <p>Gives slightly lower results compared to total iron under oxygenated conditions.</p> <p>Comparison of values for filtered iron and total iron may indicate corrosion going on nearby, upstream the sample point, if total iron is more than 150 % of filtered iron. If there is active corrosion as FAC then samples will tend towards magnetite.</p>

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Ultra-Violet/Visible (UV-Vis) Spectroscopy	Colorimetric method based on Ferrozine reaction [16] – dissolved iron only	Dissolved Fe, only as ions	100 mL (minimum size) sample bottle preserved with high purity nitric acid	9 µg/kg – using a standard 1 cm cell [17] 2 µg/kg – using a standard 5 cm cell [18]	Method unsuitable for determining the concentration of total iron corrosion products in untreated samples since it is for dissolved iron only. Method not accurate enough to be used in optimizing cycle chemistry in a plant.
UV-Vis Spectroscopy after sample digestion	Colorimetric method based on Ferrozine reaction ²⁰ after suitable digestion step where any particulate iron oxides are converted to Fe(II)-ions	Total Fe after particulate oxides are dissolved via a digestion step	100 mL (minimum size) sample bottle preserved with high purity nitric acid	9 µg/kg – using a standard 1 cm cell [18] 2 µg/kg – using a standard 5 cm cell [19]	Minimum acceptable cell length is 5 cm. Any method utilizing a 1 cm cell is ineffective due to the 9 µg/kg detection limit of 1 cm cells. Note that most commercially available portable UV-Vis spectrophotometers are supplied with 1 cm cells only. The optimum particulate iron digestion method is to add the acid to the sample and then heat it. Examples include thioglycolic acid (CH ₂ (SH)COOH) at 90 °C or boiling nitric acid (HNO ₃). Thioglycolic acid is the optimal digestion method to be used with the Ferrozine method because of its reducing effect on Fe(III).

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Atomic Absorption (AA) Spectroscopy after sample digestion	Flame-atomizer absorption spectrometry method after suitable digestion step where any particulate iron oxides are converted to Fe ions	Total Fe after digestion step	100 mL (minimum size) sample bottle preserved with high purity nitric acid	7 µg/kg [19]	High detection limit of 7 µg/kg makes this method unsuitable for determining the concentration of iron corrosion products in power plants The optimum particulate iron digestion methodology is via the addition of acid to the sample combined with heating, e.g., using boiling nitric acid (HNO ₃)
Graphite Furnace Atomic Absorption (GF-AA) Spectroscopy after sample digestion	Graphite tube atomizer absorption spectrometry after suitable digestion step, where any particulate iron oxides are converted to Fe ions	Total Fe after digestion	100 mL (minimum size) sample bottle preserved with high purity nitric acid	0.3 µg/kg [20]	Suitable for total iron corrosion products since detection limit less than optimum feedwater total iron value The optimum particulate iron digestion methodology is via the addition of acid to the sample combined with heating, e.g., using boiling nitric acid (HNO ₃)
Inductively Coupled Plasma (ICP) – Atomic Emission Spectroscopy (AES) after sample digestion	Ionization of sample then detection and quantification via emission spectrometry after suitable digestion step where any particulate iron oxides are converted to Fe ions	Total Fe after digestion	100 mL (minimum size) sample bottle preserved with high purity nitric acid	7 µg/kg [21]	High detection limit of 7 µg/kg makes this method unsuitable for determining the concentration of iron corrosion products in power plants The optimum particulate iron digestion methodology is via the addition of acid to the sample combined with heating, e.g., using boiling nitric acid (HNO ₃)

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Inductively Coupled Plasma (ICP) – Mass Spectroscopy (MS)	Ionization of sample then detection and quantification via mass spectroscopy after suitable digestion step where any particulate iron oxides are converted to Fe ions	Total Fe after digestion	100 mL (minimum size) sample bottle preserved with high purity nitric acid	1 µg/kg [22]	Suitable method for total iron corrosion products since detection limit less than optimal feedwater total iron value The optimum particulate iron digestion methodology is via the addition of acid to the sample combined with heating, e.g., using boiling nitric acid (HNO ₃)
Integrated sampling system, i.e. collection of sample (0.45 µm filter followed by ion exchange filter and known sample volume). Next acid digestion of filter and then determination of total mass of iron present on the filters.	Sample collection on 0.45 µm filter followed by an ion exchange filter at sample point operating pressure after sample cooling. Sample total filtered liquid volume recorded. Filters are then removed and digested. Total mass of iron on and in the filters determined via suitable dissolved iron analysis method such as ICP-MS, UV-Vis ferrozine method or AA. Total mass of iron is then divided by total sample volume to give average total iron concentration for the sampling period.	Total Fe after digestion of both filters	Plant operating pressure sample connection point downstream of a sample cooler. High pressure sample filter holder, high accuracy totalizing flow meter	As per iron analysis method selected	Optimal total iron corrosion products method with very low detection limit The optimum particulate filter and ion exchange filter iron digestion methodology is via the addition of acid to the sample combined with heating. Examples include thioglycolic acid (CH ₂ (SH)COOH) at 90 °C or boiling nitric acid (HNO ₃)

For copper the spectrophotometric methods are generally not sensitive enough to fulfil the purpose with detection limits larger than 5 µg/kg. ICP-OES operates down to detection limits of 1-2 µg/kg, and GFASS and ICP-MS even below 1 µg/kg. Thus, the costly instrumental methods are the preferred choice for copper.

The Babcock & Wilcox method should be used with care when both iron and copper CPs may be present as the comparison charts are developed for all-ferrous systems. Digestion of the filters and determination of both iron and copper subsequently is suggested in this case.

5.3 Proxy Methods – Turbidity, Particle Monitors, and Particle Counters

The instrumental proxy methods that have been tested for suspended particle monitoring [¹⁰] are based on turbidity, particle monitoring (a technique that gives the number of particles per volume) and particle counting (a technique that gives the number of particles per volume in several size classes, i.e. both the total number of particles and information on the particle size distribution, PSD).

5.4.1 Turbidity

Turbidity is basically the measurement of clarity of the sample. Water appears increasingly turbid with increasing amounts of suspended matter due to the scattering of light by the particles. The turbidity meters suitable for water-steam circuit application are based on the nephelometric measurement principle. In this setup, the light scattered by particles in the water is detected at an angle of 90 ° relative to the incoming beam of light. This gives a weak intensity of scattered light but also a very low background intensity. The intensity depends on the colour of the incoming light. ISO 7027 specifies that red light at 860 nm should be used whereas EPA 180.1 calls for white light in the range 400-600 nm when the turbidity is below 40 NTU (extremely high turbidity for the present application). The sensitivity is proportional to the reciprocal value of the wavelength, so instruments based on white light should be preferred for water-steam circuit applications where high sensitivity is a priority.

Turbidity is an optical property measuring the scattering from particles and thus not a direct measurement of the particle concentration in the water. The extent of scattering depends on particle concentration, but also on colour, size, and shape of the particles, and even on the refractive index of the solvent. Even ultrapure water will scatter light to a certain degree, and no solution can have a turbidity of 0 FNU (or NTU). For particles with diameters similar or slightly larger than the wavelength of the incoming light, Mie scattering will dominate. When the particle size increases, light scattered from different particles will create interference patterns that are additive in the forward direction. This means that light scattered in the 90 ° angle will increase with particle concentration, but the intensity may not increase proportionally with the concentration due to the secondary scattering effects.

The colour of the particles does also have a significant effect on the scattered light intensity. Depending on their colour the particles absorb light energy in different bands of the visible spectrum and that will prevent scattering of some of the incoming light. This means that magnetite, hematite, and copper oxide particles in water-steam samples will respond differently. The black magnetite will absorb more of the incoming white light than the red hematite that

scatters light more efficiently. The response of hematite is about three times greater than that of magnetite^b.

Turbidity is measured in units of FNU (Formazin Nephelometric Unit) or NTU (Nephelometric Turbidity Unit). Both are based on calibration with the same set of well-defined Formazin standards and are equal, i.e. 1 FNU = 1 NTU. The purest (< 1 µg/kg Fe) feedwater or rinsed condensate samples have turbidity around 0.015 FNU.

The considerations above demonstrate that turbidity is not an accurate measurement of CP concentration in the relevant sample streams, since the measured value depends not only on the particle concentration, but also on the ratio between magnetite and hematite and on the particle size that vary during transient conditions. Nevertheless, a fair correlation that allows trending of CP levels and transport and gives semi-quantitative values for CP concentration may be established. Figure 3 illustrates the relation between turbidity and filtered iron for samples from several different plant types, feed water chemistries (all oxidizing), and sampling points.

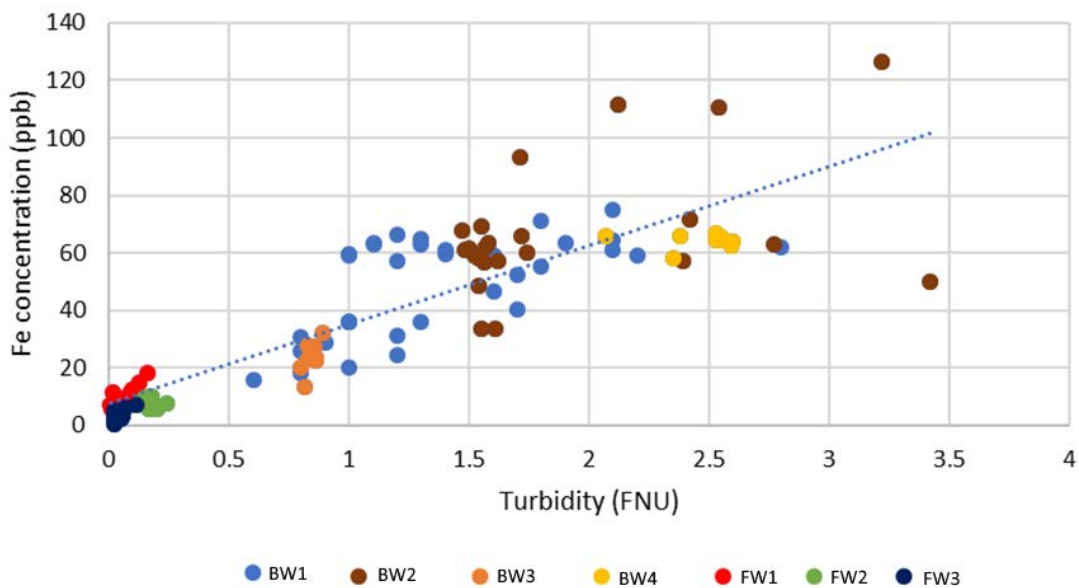


Figure 3. Relation between filtered iron concentration and turbidity under different conditions with respect to plant type (once-through combined cycle/HRSG), feedwater chemistry (AVT(O), AVT(O)+FFA, OT), and sampling point (boiler water, feedwater). The data points below 0.25 FNU represent feedwater samples whereas the higher turbidity was measured in boiler water samples.

Figure 4 displays an example of the relation between turbidity and filtered iron for a specific plant and sample point.

^b Application Note: Monitoring Iron Transport in Power Generation. 2017, Hach Company.

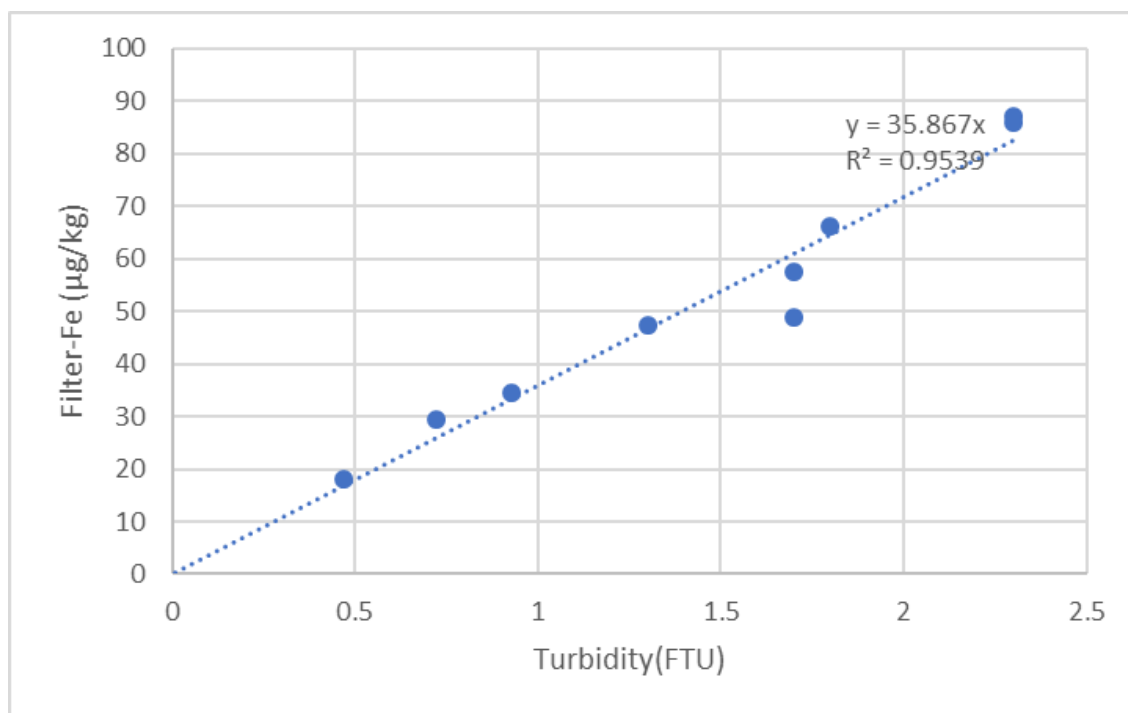


Figure 4. Correlation between filtered iron and turbidity in feedwater during a startup of a combined cycle/HRSG plant.

There is a correlation between the filtered iron concentration and turbidity, but also scatter even for the same plants. For a given plant and sampling point the relation must be established by parallel measurements, preferably over several sampling rounds covering the relevant operational situations. In that case, the uncertainty on the factor between filtered iron and turbidity may be less than 25 %, i.e. semi-quantitative iron results from turbidity may be obtained.

5.4.2 Particle Monitors and Particle Counters

Some particle monitors and particle counters rely on the shadowing effect of a particle passing an illuminated optical sensor. The light from a LED or laser diode illuminates the optical sensor across a narrow flow zone and whenever a particle passes through the flow zone, a pulse corresponding to the reduced intensity from the shadow is registered. The particle concentration is then calculated from the number of pulses per time unit and the flow rate through the zone. The particle monitors report either number of particles per minute or particles per volume (mL or L) if the flow rate is available for the instrument. The height of the pulse may be calibrated to the particle size by use of particle size standards with well-defined particle sizes. In this way, the counts may be summed up in an array representing different particle size intervals. Often, the intervals are about equal size on the logarithmic particle size scale. Particle Counters give both a total count per time or volume and the distribution across the size bins (PSD) as output. The sensing technique relying on the shadowing effect is limited by particle size, and some particle counters use forward scattered light intensity to detect and classify particles less than e.g. 2 µm. Also, the number of size bins vary for the particle counters, some have only 4 and others many (128 or even higher) allowing detailed particle size distributions to be recorded.

For optimal use the size range of both particle monitors and particle counters should be down to 0.5 µm and up to 10-20 µm to cover the relevant range. Typically, more than 90 % of hematite particles are less than 2 µm^{vi}, and instruments limited to particle sized above that seriously

misjudge the total number of particles present. Magnetite particles are larger and do not present the same problem for this type of instruments.

The particle monitors are subject to limitations regarding the correlation between particle concentration and corrosion product concentration because the particle size is not considered. The concentration of iron or copper is proportional to the median diameter in the third power. This means that the concentration found by chemical analysis is extremely sensitive to the particle size that is expected to vary with the operating conditions such as transient load. Typically, the median particle size increase under such conditions, and the correlation to the particle concentration will underestimate the concentration. As with turbidity, only a semiquantitative relation between CP concentration and the particle monitor response may be established.

The particle counters ideally register the PSD, and the median diameter may be calculated for each measurement. Thus, the influence of varying particle size with operating conditions can easily be considered when comparing with either filtered CP or total CP analyses. The key point here is that the particle size interval evaluated should match the particle size distribution of the sample.

5.4.3 Relation between Proxy Methods and Chemical Analysis

As demonstrated by Figure 3, an approximately proportional relation exists between filtered iron and turbidity. The proportionality coefficient depends on particle size, color of the CPs, and even the number of particles per volume, i.e. the conditions defined by the local feedwater chemistry at each site. Thus, the relation must be established under the given conditions for the best possible conversion between turbidity (or numbers from particle monitors) and filtered iron. This is optimally done by accumulating parallel measurements of turbidity (or particle monitor counts/volume) and filtered iron over several series of samples to record the day-to-day variation also. Such data allows for a reliable estimate of the proportionality coefficient and the associated uncertainty (as a relative standard deviation) that will be the governing uncertainty when converting proxy data to estimates of iron concentration.

Particle counters gives additional information on the PSD of the CPs in the sample. With some basic assumptions on chemical composition and porosity of the CPs, this allows calculation of the CP concentration. As an example, the iron concentration may be estimated by the equation:

$$[Fe] = w\% \cdot \rho \cdot (1 - p) \cdot \frac{\pi}{6} \cdot d^3 \cdot N \cdot k$$

where	[Fe]	is the calculated concentration of iron ($\mu\text{g}/\text{kg}$)
	w%	is the weight percent of iron in the oxide ($\sim 72\%$ for both magnetite and hematite).
	ρ	is the density of the iron oxide ($\sim 5.2 \text{ g}/\text{cm}^3$ for both magnetite and hematite).
	p	is the porosity of the iron oxide (~ 0.15 as a qualified estimate).
	d	is the median diameter (μm) as calculated from the PSD
	N	is the number of particles per volume (units $1/\text{mL}$ or $1/\text{L}$)
	k	is a conversion constant depending on the units of N (1 or 10^{-3} , respectively)

Parallel measurements of turbidity and particle number/PSD may show the limitations of turbidity as a proxy technique [23]. Figure 5 shows the relation between turbidity and total particle concentration during a transient load situation for a once-through boiler on OT.

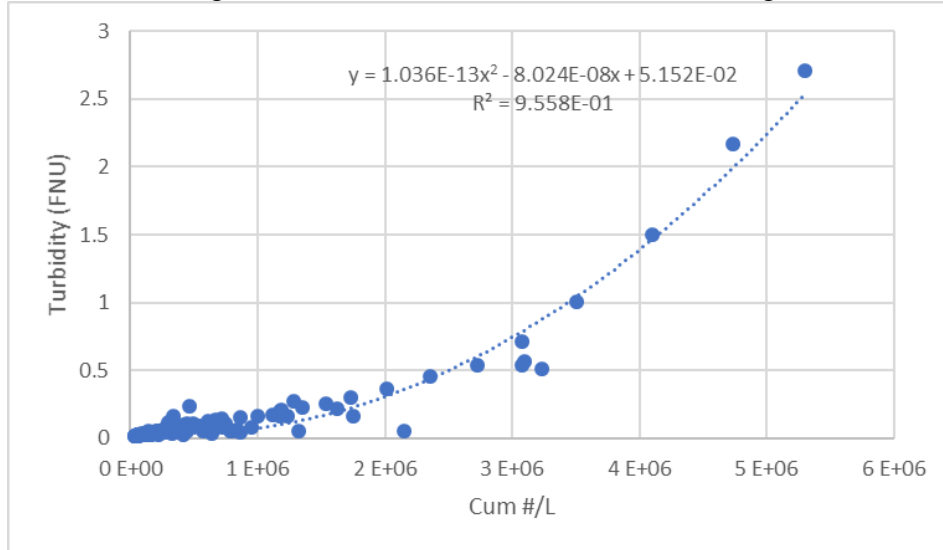


Figure 5. Corresponding measurements of turbidity and total number of particles/volume in feedwater of a once-through fossil plant operating on OT. The data set was recorded during a load transient of a once-through boiler on OT where the load increased from 30 to 60 % over a 10 min period.

The relation appears linear up to $\sim 2 \times 10^6$ particles/L then gradually shifts to a quadratic relationship, most likely from secondary scattering effects.

The dependency of the turbidity of the particle size may be estimated by calculating the ratio between turbidity and concentration from the PSD. Figure 6 displays this ratio versus the mean particle size during the transient load situation.

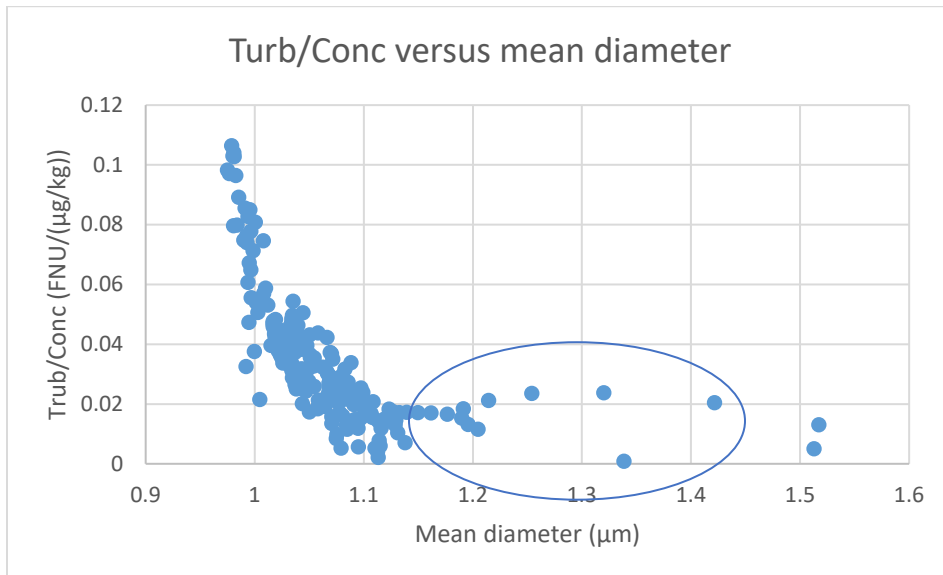


Figure 6. The effect of particle size on turbidity. Turbidity has been divided by the concentration calculated from the PSD to eliminate the effect of particle numbers. The data set was recorded during a load transient of a once-through fossil boiler on

OT where the load increased from 30 to 60 % over a a 10 min period. The circled data represents the peak of the transient with iron concentrations above ~50 µg/kg.

The figure illustrates that the turbidity depends rather strongly on the particle size because of the effect on Mie scattering.

The two effects that cause deviation from proportionality between turbidity and iron concentration counteract each other to some extent. This is illustrated in Figure 7 that shows the relation between calculated concentration and turbidity.

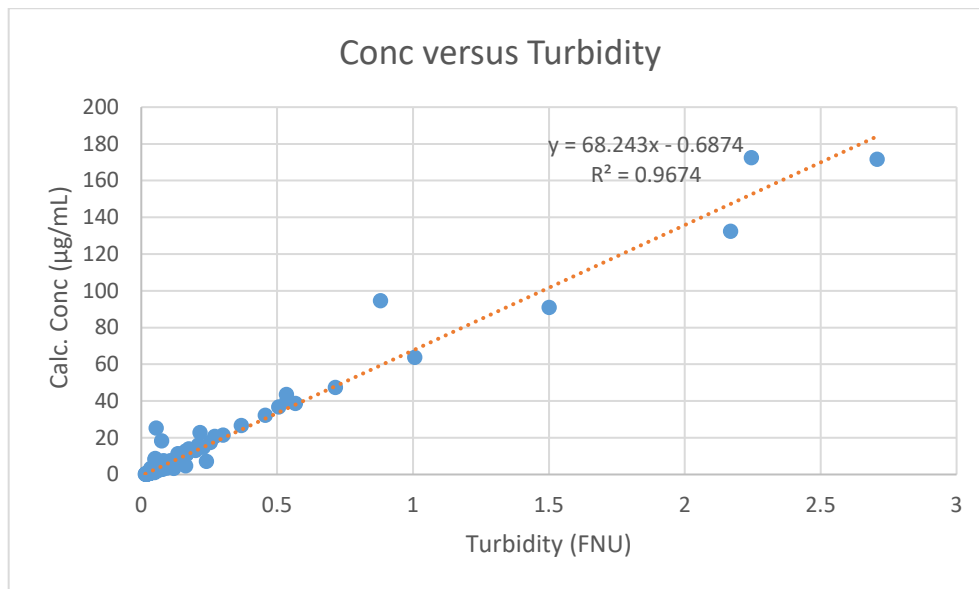


Figure 7. Relationship between iron concentration calculated from PSD and turbidity. The data set was recorded during a load transient of a once-through fossil boiler on OT where the load increased from 30 to 60 % over a a 10 min period.

The proportionality between iron concentration and turbidity seems to be good up to around 0.5 FNU then an increasingly negative effect from the dependency of particle size is observed.

6. Application of Proxy Methods

The applications described in this section covers mainly monitoring of iron oxides, since experience so far has been gathered in all-ferrous systems. The description may be used as inspiration for monitoring CPs in mixed-metallurgy systems.

6.1 Purposes of On-Line Monitoring

The reliable monitoring of particle levels by means of the proxy methods – even if the relation to iron or copper concentration is only semiquantitative – opens new possibilities for:

- Evaluation of oxide transport during the operational phases when it is elevated
- Optimizing processes when spikes of particles appear.

6.2 Corrosion Product Transport during Startup

The evaluation of CP levels and transport during startup is a primary means to investigate if the chemical conditions during operation, shutdown and outages are optimal. Suboptimal shutdown

procedures and incomplete preservation during shutdown will invariably increase the amount of CPs circulating during the next startup. Improvements of the chemical conditions during these phases and operation will be reflected in significantly lower concentrations of CPs in the following startup. This will not only improve the integrity of the components but also lead to faster startups and a corresponding cost reduction. The sampling point of choice is the economizer inlet as this allows measuring the CP amount transported to the boiler or HRSG evaporator during startup. Combined cycle/HRSG plants often use the HP evaporator drum water as another key sampling point for CP monitoring. The CP level observed here is a balance between the amount carried in with the feedwater, accumulation by evaporation, and the amounts removed by blowdown and deposition on surfaces.

The procedures for evaluation of the startup data is described in Section 7, and the guidance concerning this optimization is treated in Section 8.

6.3 Oxide Transport during Cyclic Load

With proper feedwater conditioning the CP levels in the circuit during steady-state operation should be very low. However, during transient conditions such as load changes, peaks of CPs appear both in the condensate and feedwater, most likely because deposited particles are brought in suspension by the turbulence caused by the changes in the main flows. For plants that frequently operate with in a cycling mode, the traditional analyses of CPs under high load, steady-state conditions will not give a good picture of the transport of oxide particles to the boiler/evaporator. Most of the particulate matter is transported into the boiler during load changes when chemical analyses traditionally are not performed. Grab sampling during such conditions seldom gives the full picture because the levels of oxides change quickly. The proxy techniques allow keeping an eye on the transport of CPs and in some cases exfoliated oxides originating from superheaters of high alloyed materials during transient loads, e.g. by observing:

- Transport of oxides (CPs and exfoliated oxides) to boiler/evaporator
- Level of oxide particles in boiler water
- Deposit on and cleaning effect of condensate filters

Sampling locations: Economizer inlet, boiler water, condensate(s)

6.4 Optimizing Processes Based on On-Line Proxy Methods

Depending on the materials, superheaters may contribute to the iron oxides observed during cyclic load/transient conditions. On-line measurement of the oxide levels may be used actively to improve the processes by for instance:

- Controlling the blowdown rate from drums and evaporators to keep the circulating oxides at the lowest level possible. Along with the other criteria for blowdown (conductivity or CACE) this allows optimal blowdown and minimum loss of energy.
- Divert process condensates from district heating or external processes to CPP or condensate filters. Such condensates are often taken back into the condensate train after LP heaters from energy consideration and diverting them to filtration only when necessary, saves energy and reduces the amount of iron oxides transported into the feedwater.

6.5 Summary of Rationale and Sampling Locations

The previous subsections have indicated the most important applications of CP analysis for flexible plants, and Table 5 summarizes the sampling points using the abbreviations:

- CPT/SU – Corrosion Product Transport during Startup
- ToO/CL – Transport of Oxides during Cyclic Load
- PC/CL – Process Control during Cyclic Load.

Table 5 - Summary of key corrosion product sampling locations for flexible operation

Type of Plant	Sampling points						
	ACC Outlet*	Condensate Filter Outlet*	Condensate Pump Discharge	Process Condensate Return	Dearator Inlet	Economizer Inlet	Boiler /Evaporator
Conventional – All Ferrous	CPT/SU	ToO	CPT/SU	ToO PC/CL	(ToO)	CPT/SU	ToO PC/CL
Conventional – Mixed Metallurgy							
Combined CC/HRSG Plants	CPT/SU	ToO	CPT/SU	ToO PC/CL	(ToO)	CPT/SU	ToO PC/CL
Cogeneration Plants	CPT/SU	ToO	CPT/SU	ToO PC/CL	(ToO)	CPT/SU	ToO PC/CL

* If ACC or condensate filters installed, (ToO/CL): Use to track several contributions in condensate system,

7. Monitoring Startup

This section covers the procedure for monitoring CP levels and transport during startup and gives guidance on the data treatment.

7.1 Procedure for Monitoring Startup

This procedure is the preliminary version of the version which will finally be in the IAPWS TGD.

Proxy techniques

- Turbidity, particle monitoring or particle counting – i.e. methods suited for data acquisition. Recording of data with at least 1 minute resolution. The methods are described in Section 5 of this document
- Babcock & Wilcox Membrane Filter Method – possibly in combination with the filter method, i.e. digestion and analysis afterwards. This method is possible but labor intensive. These methods are described in Section 4 of this document.

Preparation

- Open the sample line and start flushing as soon as the feedwater pump is in operation and gives pressure. In the beginning flush the sample line directly to drain until the first burst of particles/deposits has been flushed out. Then regulate the sample flow to the lowest flow giving turbulent conditions and keep flushing. The flow will gradually increase as feedwater pressure builds up.
- Attach the proxy instrument or open the valve to a permanent installed instrument. Adjust the sample flow to the proper setting by means of the constant head device upstream the instrument.
- Prepare sample bottles for filtered iron, if this is the proxy method of choice. This will require 20-30 bottles. Otherwise, around 10 samples will be taken in parallel. Alternatively, load the filter holders with filters so they are ready for use. It is an advantage to have several, so that there is time to change filters without time pressure.
- Check the sample flow as feedwater pressure is established, it may be necessary to reduce flow not to overload the sample cooler or the constant head device.

Measurement

- Start measuring at first fire and continue when the feedwater pressure builds up. Time of first fire is the starting point for measurements, so this should be precisely recorded.
- Note the time for start of bypass operation (if applied at the plant), turbine runup and steam turbine and/or generator synchronization.
- Watch the monitor response – most likely, the CP level increases towards a maximum and then starts decreasing in a slow decay. Note, the maximum value, and then take filter samples from the bypass line of the constant head device for each 10 % change noting the exact start time and monitor output when sampling starts and stops.
- If no monitor is applied, take samples for each 5 % change or each 10 minute period noting the exact start time when sampling starts and stops. The idea is to take samples covering the slow decay towards the steady-state level.

Analysis

- Digest and analyze samples taken in parallel with the on-line monitor.
- If no monitor is applied, estimate the iron content from the color of the filters by comparison with the Babcock & Wilcox Membrane Filtration Charts. Save the filters for analysis later if the initial evaluation makes sense. (**Note: there has been some discussion among the IAPWS STG on this topic because of the large gaps between values on these charts. Discussion will continue to finalize the IAPWS position).

7.2 Evaluation of Startup Data

Monitor response recorded

- Estimate the factor (see Section 5.3) between average detector response and filter iron during each sample period from a plot of filter iron versus response. If the factor has been evaluated earlier, aggregate the present values with that earlier to expand the statistical base for the factor.
- Scale the recorded monitor response to filter iron ($\mu\text{g}/\text{kg}$) by means of the estimated factor.

Construct the decay plot

- Plot the filter iron ($\mu\text{g}/\text{kg}$) either from the scaled monitor response or from filter analysis versus the time after first fire using a log-scale on the y-axis. Figure X depicts the expected curve in this plot.
- Mark the milestones of the startup on the plot, e.g. bypass operation, turbine runup, and synchronization.
- Estimate the time since first fire to reach the steady-state or acceptable level (whichever comes first) of oxides in feedwater.
- Estimate the half lifetime for the decay from the largest peak towards the steady-state value from the graph.
- Estimate the area under the curve from time of first fire to time of steady-state. This is most easily done by numeric integration of the dataset behind the curve, i.e. by calculating the sum:

$$Fe_{trans} = \frac{1}{2}\Delta t * Q_{fw} * (R_0 + R_n + 2 * \sum_{i=1}^{i=n-1} R_i) * 10^6 \mu\text{g}/\text{g}$$

Here:

Fe_{trans} is the iron transported in g

Δt is the time resolution of the responses in s

Q_{fw} is the average feedwater flow during the decay in kg/s

R_0 and R_n are the first and last scaled response value corresponding to first and last response, respectively

R_i are the scaled response values between the first and last response value, i.e. the response values for $i = 1..n-1$

- If no monitor has been used, plot a curve of the product of filtered iron and feedwater flow at the sampling time versus time after First Fire, draw a smooth curve through the data points and estimate the area by the "cut-and-weigh" method. i.e. cut the area under the curve out and weigh it. The area may then be found as the ratio between the weight of the area and a rectangle corresponding to constant filtered iron content, constant feedwater flow, and a known time span.

Figure 8 shows an example from a combined cycle/HRSG plant starting up after a summer shutdown with dry air preservation of the boiler. The amount of iron transported to the HP

evaporator from First Fire to stable, low iron level was 4.3 g as calculated from the formula above. The turbidity was converted to filtered iron by means of the correlation shown in Figure 4.

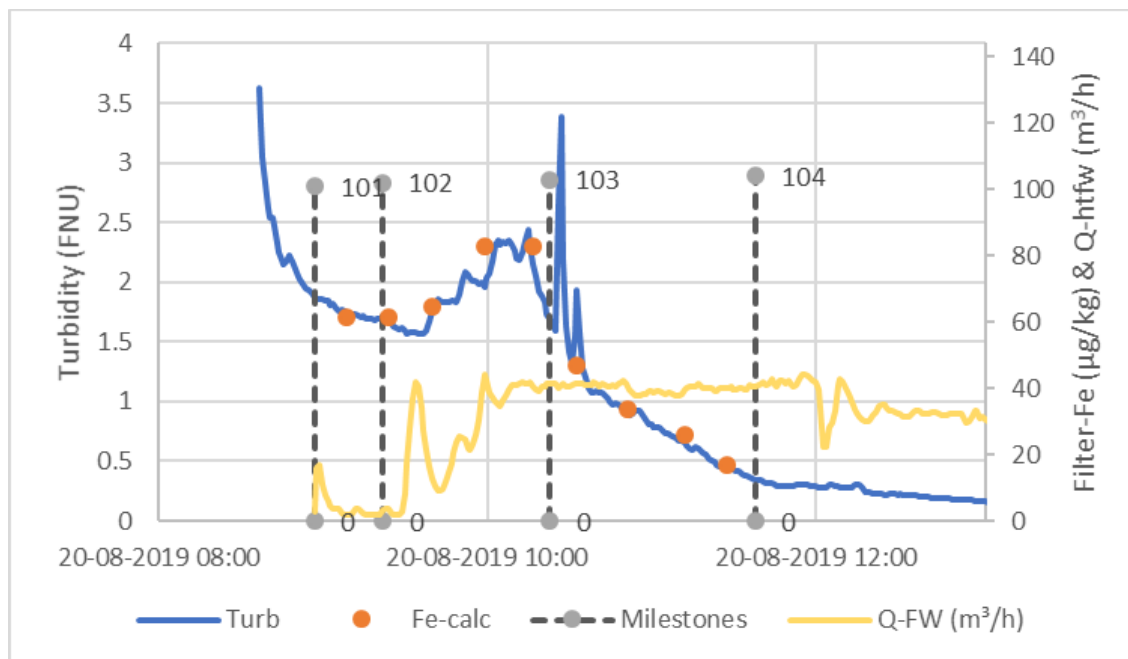


Figure 8. Turbidity and filtered iron measured during startup of a combined cycle/HRSG plant. The milestones marked are: 101: GT fire, 102: Heating of deaerator tank, 103: Addition of makeup water, 104: Steam turbine synchronization.

8. IAPWS Guidance for Corrosion Product Generation and Transport for Fast Start and Frequently Started Units

8.1 Introduction to the IAPWS Corrosion Product Decay Maps.

The previous sections of this IAPWS White Paper have described the sampling, monitoring and analysis approaches for monitoring iron and copper in frequently started and fast starting conventional and combined cycle/HRSG plants. This section provides operators with IAPWS guidance on how to interpret the results in terms of whether the operational and shutdown/layup chemistries of the plant are optimum or not.

One of the first studies of the decay of iron and copper corrosion products during startups was conducted in the 1970s [24]. This showed for frequently started mixed-metallurgy fossil units that immediately following unit startup the corrosion product levels elevated to a peak and then, depending on the operational and shutdown chemistries, took up to many hours to decay to normal steady state values. The same trends have also been demonstrated in other plant studies [25]. Additional work [26] with all ferrous conventional plants operating under AVT(O) and OT conditions in the early 2000s produced similar results that demonstrated lower corrosion product transport on startups with OT compared to AVT(O). These observations have now been developed into the IAPWS Corrosion Product Decay Maps to allow operators to review the results of the proxy analyses described in the previous sections of this White Paper (pre-TGD). The concept is summarized in Figure 9. (**Note: this is a preliminary draft figure. The STG will discuss further and iterate to a final version).

CONCEPT FOR IAPWS PRODUCT DECAY MAP

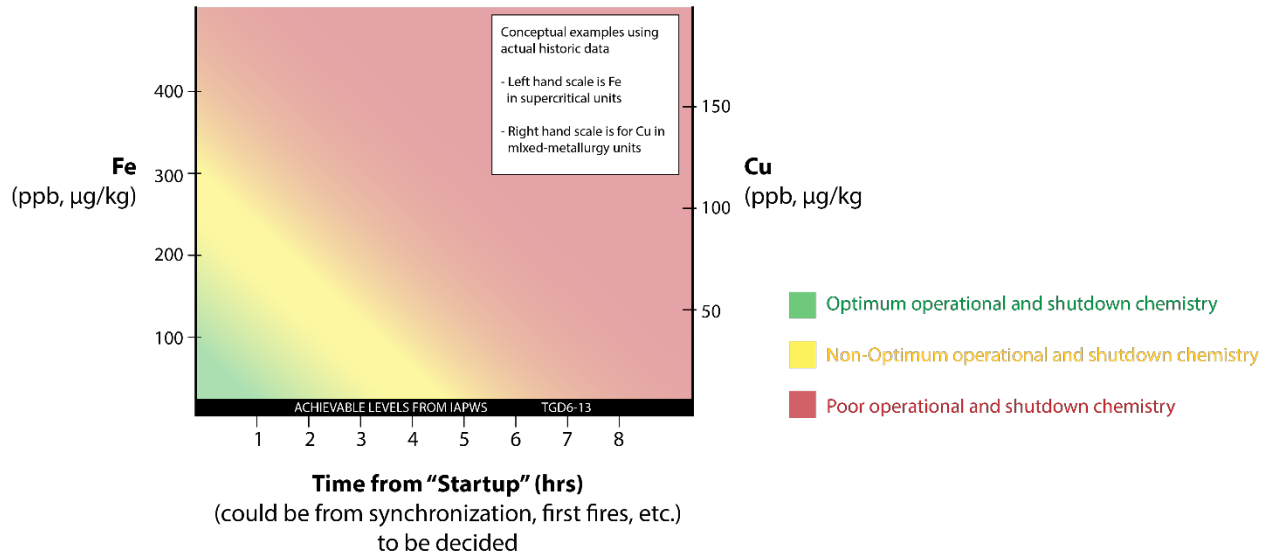


Figure 9. The IAPWS Corrosion Product Decay Map (concept at this stage). In Section 7 the starting point is defined as First Fire.

8.2 The IAPWS Base Cases for Decay of Corrosion Products

The IAPWS TGD for Volatile Treatment first introduced base cases and tables of cycle chemistry limits which cover the most common units and cycle chemistries in use around the world in conventional plants and multi-pressure combined cycle/HRSG plants. The same concept has been continued in all the subsequent IAPWS TGDs and are adopted in this White Paper (pre-TGD) with some slight modifications needed for interpreting corrosion product decay after startup. The three base cases address units with all-ferrous feedwater systems operating with oxidizing chemistries (AVT(O) and OT).

- Base Case 1. Conventional and biomass plants with once-through subcritical and supercritical units, non-copper-tubed condensers and a condensate polisher;
- Base Case 2. Conventional and biomass plants with drum units, with drum pressure up to 20 MPa (~2900 psi), non-copper-tubed condensers and with a condensate polisher.
- Base Case 3. Multi-pressure combined cycle/HRSG drum units, with either independently fed LP, IP and HP circuits or with the LP drum feeding the IP and HP circuits. These base case units do not have a condensate polisher. The drum pressures on this base case are considered to be LP 0.5 MPa (70 psi), IP 2.4 MPa (350 psi), and HP up to 17 MPa (2500 psi).

As described in Section 6, the normal sampling point for each of these base cases is at the economizer inlet (EI) for the conventional plants and at the boiler feedpump exhaust for the combined cycle/HRSG plants, which is essentially the inlet to LP, IP or HP economizer. As indicated in Section 6.2 for the combined cycle/HRSG plants the drum/evaporator water is also a key monitoring point for CPs. Additional sampling points are suggested for some of the customization cases in Section 6 and 10.

If a plant does not fit the characteristics of the three base cases, then the reader is directed to Section 9 where guidance and interpretation are provided on corrosion product levels and decay

following startup for several other plants. The operator or chemist should first determine which variation(s) is closest to their plant and then will be able to customize the operational plant chemistry and shutdown protection to minimize the corrosion product transport.

8.3 The IAPWS Corrosion Product Decay Maps for the Three Base Cases.

Once an operator or chemist has conducted the sampling and analysis of corrosion products as delineated in Section 7 and has produced a decay profile such as shown in Figure 8, then there is need to determine if this profile represents the lowest level of transported corrosion products, or if improvements can be made to the operational chemistry or shutdown protection provided. The IAPWS Decay Maps provides this guidance by comparing the actual decay profile with the lines and coloured areas of the Map. (**Note: original versions of the Decay map included lines as boundaries to the coloured areas. These were removed in the version in Figure 9. The STG will discussion the final format required and decide whether to include actual lines as boundaries or keep as “hazy” areas between the coloured areas. The remaining text will then be finalized)

Figure 9 shows the IAPWS Corrosion Product Decay Map. The map has been constructed based on: a) an IAPWS International Collaborative Project involving plants in Denmark, UK, Australia and New Zealand, b) the wide experience of IAPWS members worldwide, and c) literature on monitoring corrosion products in cycling plants [^{23, 25, 26}]. The Map shown in Figure 9 shows iron and copper corrosion product decay; the iron decay relates to the three base cases in Section 8.2, and for mixed-metallurgy units with copper alloys in the feedwater which is discussed in Section 9.2. Because each unit is different in terms of equipment, surface area, operating and shutdown/layup chemistry, it is emphasized that while there are coloured areas on this Map, the reader should be more interested in the reasons that plants can achieve the lowest corrosion product transport levels or monitor severely high transport levels. Some of these are outlined in the three following sub-sections. A few notes of initial guidance can be identified:

- i) A band representing the normal achievable levels for these units has been drawn on the map from the IAPWS original TGD for corrosion products [¹].
- ii) The “area under the curves” (such as in Figure 8) represent the total amount of corrosion products that are transported and can deposit on to the boiler waterwalls or HRSG HP evaporators. Thus, not only the height of a curve (elevated level of corrosion product) but also the length of time that there is elevation are both most important. The higher an organization’s profile relates to the IAPWS map, the worse is the operational chemistry and shutdown/layup shutdown conditions. Review of the factors in Section 9.4 will direct the operator to improvements in both. (**Note: The formula and descriptions in Section 7 can be used along with feedwater flow to calculate the area under the curve. The STG will discuss and provide final Guidance.)
- iii) The green area on the map should be the goal for plants when operating and shutting down units optimally. Monitored levels above these should trigger work to improve both factors. These are delineated in Section 8.4.
- iv) The yellow or red areas are examples of much poorer operational and shutdown chemistries. To reduce the risk of heavy conventional plant waterwall and HRSG HP evaporator deposits and under-deposit corrosion [^{27, 28, 29}], an operator should aim to have profiles from the Fe/Cu monitoring using the proxy method as low as possible in the green area.

- v) The total levels of corrosion products (area under the curve) are dependent on the operational chemistry, the length of a shutdown and the rate at which a unit is brought back into service. See Section 9.5 under Customization.
- vi) The time to reach “approximate achievable IAPWS levels” is also very important. The IAPWS experience is that a corrosion product decay profile at the top of the yellow area or in the red area will never reach these levels.
- vii) The Map and Section 8.4 should be used to develop lower corrosion product transport rates by changing the operational or shutdown/layup chemistry to more optimum.
- viii) (**Note: Further discussion is needed by STG on whether the White Paper includes one Map or a number of maps for each base case)

8.4 Influencing Factors for Corrosion Product Decay for the Three Base Cases.

Section 8.3 has described the results that can be achieved by comparing an organization’s Corrosion Product Decay profile with the IAPWS Map. This section provides outlines of the factors that result in those profiles representing low corrosion product transport (Green area) or representing much higher corrosion product levels which will ultimately result in failure and damage for the plant (red area).

8.4.1 Supercritical Units (Base Case 1)

Indications of optimum chemistry control on these units (corrosion product profiles in the Green area):

- Optimum OT chemistry for supercritical and ultra-supercritical plant is as described in the IAPWS Volatile TGD [4]
- One injection point for oxygen at CPD
- During operation – vents on LP and HP heaters, and on the DA closed
- Plant has good air in-leakage (AIL) control and an AIL Plant team [30]
- Downstream of control valves on feedwater heater drains and emergency drains checked for FAC as well as locations on heater shells where cascading drainage enters [31]
- No change of chemistry during shutdowns such as increase of pH which is not needed for oxidizing cycles for shutdowns up to about a week. Normal operational chemistry can be maintained for a number of weeks.
- During longer shutdowns (more than a week) the surfaces are protected with N₂ blanketing, DHA, by pH elevation, or by the use of FFS during operation [32]
- Others to be added

Indications of non-optimum chemistry on these units (corrosion product profiles in the Red area)

- OT chemistry for supercritical and ultra-supercritical plant does not follow the IAPWS Volatile TGD [4], with vents on heaters and/or DA not fully closed or leaking.
- Poor AIL control and no AIL plant team [30]
- Continued use of AVT(O) with insufficient oxygen to completely passivate all the feedwater surfaces [4] resulting in ruggedly red surfaces

- Use of AVT(R): (IAPWS is aware that some supercritical units worldwide operate with AVT(R) due to a complete misunderstanding that the oxide growth and exfoliation in steam is influenced by oxygen levels [12]).
- No short-term or long-term shutdown/layup protection using N₂ blanketing, DHA, or by the use of FFS during operation [30].
- Leaving water circuits standing in wet aerated conditions and unprotected during shutdowns by:
 - Breaking condenser vacuum after unit shutdown whilst continuing to forward condensate / feedwater;
 - Addition of oxygenated water to the water-steam circuit during shutdowns without appropriate chemical conditioning;
 - Not using FFS during operation or pH elevation during shutdowns to compensate.
- Others to be added

8.4.2 Drum Units (Base Case 2)

Indications of optimum chemistry control on these units (corrosion product profiles in the Green area):

- Optimum AVT(O) or OT chemistry is as described in the IAPWS Volatile TGD^{iv}
- If operating on OT during operation – vents on LP and HP heaters, and on the DA closed. One injection point for oxygen at CPD.
- Plant has good air in-leakage (AIL) control and an AIL Plant team [30]
- Downstream of control valves on feedwater heater drains and emergency drains has been checked for FAC as well as locations on heater shells where cascading drainage enters [31]
- No change of chemistry during shutdowns such as increase of pH which is not needed for oxidizing cycles for shutdowns up to about a week. No change to AVT(R) during shutdown
- During longer shutdowns (more than a week) the surfaces are protected with N₂ blanketing, DHA, by pH elevation, or by the use of FFS during operation [32]
- Water circuits are periodically circulated during longer-term shutdowns to prevent localised corrosion cells becoming established.
- Others to be added

Indications of non-optimum chemistry on these units (corrosion product profiles in the Red area)

- Continued use of AVT(R) chemistry with addition of a reducing agent (see Section 9.1)
- AVT(O) or OT chemistry does not follow the IAPWS Volatile TGD [1], with vents on heaters and/or DA not fully closed if using OT.
- Poor AIL control and no AIL plant team [30]
- Use of reducing agent during shutdown when operational chemistry is AVT(O)

- Continued use of AVT(O) with insufficient oxygen to completely passivate all the feedwater surfaces [4]
- Conversion to AVT(R) during shutdown.
- No short-term or longterm shutdown/layup protection using N₂ blanketing, DHA, by pH elevation, or by the use of FFS during operation [30]
- Leaving water circuits standing in wet aerated conditions and unprotected during shutdowns by:
 - Breaking condenser vacuum after unit shutdown whilst continuing to forward condensate / feedwater;
 - Addition of oxygenated water to the water-steam circuit during shutdowns without appropriate chemical conditioning;
 - Not using FFS during operation or pH elevation during shutdowns to compensate.
- Units shutdown with elevated levels of contaminants in water circuits, e.g. chloride and sulphate above normal recommended boiler water targets.
- Others to be added.

8.4.3 Combined Cycle/HRSG Plants (Base Case 3) (**Note: Currently the IAPWS Maps relates to feedwater corrosion products. STG needs to discuss whether to develop a Map for Drum CPs)

Indications of optimum chemistry control on these units (corrosion product profiles in the Green area):

- Use of AVT(O) chemistry (or much rarer OT) which follows the IAPWS Volatile TGD^{iv}
- Use of PT or CT for the drums and evaporators which follows the IAPWS Alkali TGD^v
- Single- and two-phase FAC assessments have been made for typical areas of FAC in HRGS [8, 31]
- Low levels of HP Evaporator Deposits according to IAPWS TGD (< 15 mg/cm² or within the green/yellow band on IAPWS TGD7-16 HRSG HP Evaporator Deposit Map) [7]

Indications of non-optimum chemistry on these units (corrosion product profiles in the Red area):

- Use of AVT(R) chemistry [4]
- Incorrect usage of PT or CT [14]. In the former, this might involve using other than tri-sodium phosphate or an unknown proprietary phosphate blend.
- High levels of HP Evaporator Deposits according to IAPWS TGD (> 25 mg/cm² or within the red band on IAPWS HRSG HP Evaporator Deposit Map [7])
- Poor AIL control and no AIL plant team [30]
- No Shutdown protection (N₂, DHA, FFS). Multiple cases. For example: a) changing from operating in a 2X1 mode (two gas turbines and two HRSGs) to 1X1 mode (with one GT and HRSG in service) which requires protection for the shutdown HRSG, or b) waiting for system control (initially X days/hours shutdown moves to multiples of X).
- Others can be added.

9. Customization and Understanding of Corrosion Products and Decay Profiles for Units other than the Base Cases

As with the other IAPWS TGDs, this customization section is most important so that the understanding of corrosion product transport and decay profiles following startup can be used to improve or optimize the operational chemistry and shutdown/layup procedures. This will importantly reduce the generation and transport of corrosion products to locations where they initiate damage/failure. The IAPWS Guidance in Section 8 has been developed for the three base cases representing most of the plants worldwide which are required to start frequently and or be required to start quickly. The vast experience of the IAPWS community has been surveyed to provide the additional guidance in this section for units that don't fit into the base cases in Section 8. So, this Customization Section provides guidance for units operating with non-optimum chemistries such as units with all-ferrous feedwater systems using a reducing agent and operating with AVT(R), and units with mixed-metallurgy feedwater systems operating with an oxidizing chemistry. Mention is also made for units having a copper-tubed condenser. Guidance and interpretation are also provided for units with air-cooled condensers (ACC) and those operating with Film Forming Substances (FFS). The length of shutdown periods is also of importance in controlling the level of corrosion products generated and transported.

The previous sections of this document have provided general guidance for the base cases. **However, it is emphasized again that this is an IAPWS Technical Guidance Document and that, depending on local requirements, the proxy methods for sampling and monitoring corrosion products and the guidance for the interpretation of the corrosion product decay profiles will need to be adapted and customized for some plants as there cannot be one set which can be applied to every plant worldwide.**

9.1 Conventional Drum Units with All-ferrous Feedwater Systems Operating with Reducing Chemistry.

Although it is very clear in the IAPWS TGD [4] that units with all-ferrous feedwater systems should operate only with oxidizing feedwater treatments [4], there are still over 35% of these units worldwide continuing to operate with AVT(R) [8]. This means that the carbon steel surfaces throughout the feedwater system are not protected or passivated resulting in increased levels of corrosion products with decay profiles outside of the green area in Figure 9. It is also well understood that the possibility of single-phase FAC increases drastically when these units operate under reducing conditions. The factors contributing to this are very similar to the factors delineated in Section 8.4.2 for non-optimum chemistry.

Indications of non-optimum chemistry on these units (corrosion product profiles in the Red area):

- Continued use of AVT(R) chemistry with addition of a reducing agent
- Poor AIL control and no AIL plant team [30]
- Use of reducing agent during shutdown when operational chemistry is AVT(O)
- Conversion to AVT(O) during shutdown, because
- no short-term or longterm shutdown/layup protection using N₂ blanketing, DHA, by pH elevation, or by the use of FFS during operation [32]

- Others can be added.

9.2 Conventional Drum units with Copper Feedwater Systems

This sub-section is generally applicable to older units with copper alloys in the feedwater. Thus, these units are rarely those required by system constraints to start rapidly. But these units are now often frequently started, and this is a critical operating regime for copper alloys in the feedwater and boiler water. Protection of these copper alloys during shutdown/layup is equally important in controlling the transport of the copper oxide corrosion products. Generally, the corrosion of conventional plant feedwater copper-based alloys and the transport of copper oxides increases with oxygen concentration (increasing ORP) under AVT chemistry [33]. This involves a continued growth of cupric oxide on the copper alloy as oxide is removed from the surface and the base metal continues to corrode. There is a risk for cupric and cuprous oxide release, transport, and re-deposition in the feedwater and generating sections. Pure copper will deposit on internal boiler waterwall surfaces. There is then the threat of copper hydroxide (cupric and cuprous) formation in the boiler under oxidizing shutdown conditions. This leads to volatilization and transport through the superheater and to the steam turbine sometimes resulting in serious deposition and performance loss. The accepted international protocols for mixed-metallurgy feedwater systems, as outlined in the IAPWS TDG for Volatile Treatments [4], should be applied in order to minimize these risks.

It is quite common for units with all-ferrous feedwater systems to have condensers with copper alloy tubing. In these cases, IAPWS suggests that the sampling and monitoring according to the proxy method (Section 7) are applied at the condensate pump discharge sampling location as well as at the economizer inlet for conventional plants. Also, many units are mixed-metallurgy in the LP feedwater system and all-ferrous in the HP feedwater system; in these cases, IAPWS advocates monitoring copper at the deaerator inlet.

A typical copper oxide corrosion product decay curve is shown in Figure 10 based on actual data [24] from a frequently started unit with a mixed-metallurgy feedwater system. Interpretation of this behaviour can be treated in the same ways as for the base cases in Section 8.

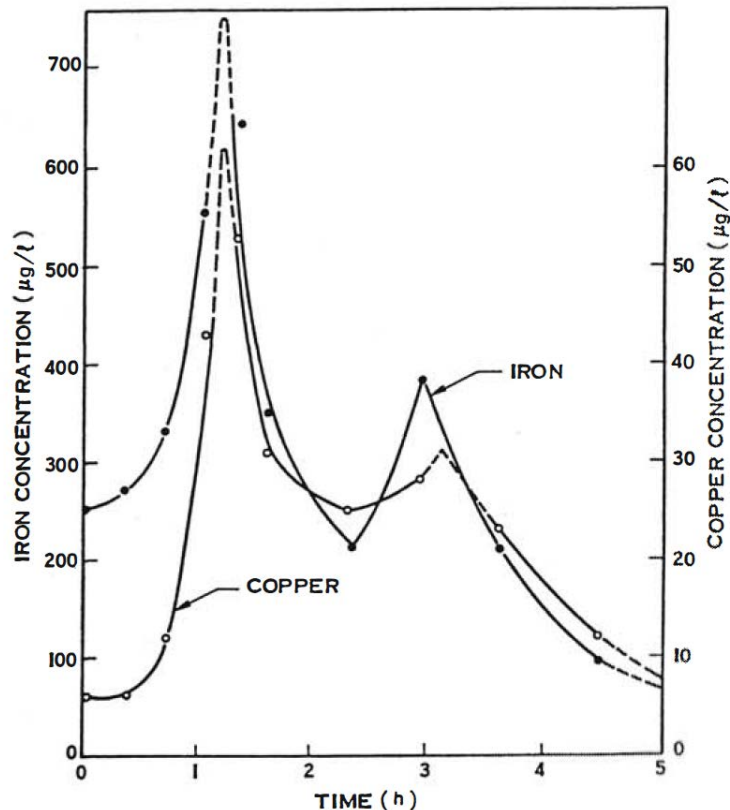


Figure 10. Release of iron and copper oxides following a startup of a mixed-metallurgy unit [24]. The time scale is relative to synchronization in this case.

Indications of optimum chemistry control on these units (corrosion product profiles in the Green area):

- Optimum AVT(R) chemistry is as described in the IAPWS Volatile TGD [4] and [33]
- AVT(R) during operation means low oxygen levels (<10 ppb, µg/kg) in the LP feedwater system with the addition of a reducing agent at the condensate pump discharge.
- Plant has good air in-leakage (AIL) control and an AIL Plant team [30]
- During shutdowns longer than overnight the feedwater chemistry remains on AVT(R) and the feedwater is protected with nitrogen blanketing or through the use of a FFS during operation [30]. It is also of paramount importance to provide shutdown protection to the boiler during these shutdowns to prevent/minimize the transition of copper deposited on the waterwalls to cupric hydroxide.
- Others can be added

Indications of non-optimum chemistry on these units (corrosion product profiles in the Red area):

- Non-optimum AVT(R) chemistry means that the factors immediately above are not adhered to. The key indication is that AIL is not under control and the oxygen levels in the condensate and LP feedwater system are high (> 20 ppb, µg/kg). No shutdown protection is provided to the feedwater system and boiler, and a FFS is not used during operation.

- Others can be added.

9.3 Units with ACC

An increasing number of plants worldwide in all categories are equipped with air-cooled condensers (ACC); they are also common equipment in industrial plants. Operating units with ACC at the lower regimes of pH provided in IAPWS Volatile TGD [4] may result in serious corrosion and FAC in the ACC tubes, most predominantly at the entries to the cooling tubes [36]. Whether this is occurring can easily be determined by monitoring the total iron at the condensate pump discharge (CPD) [31]. The most recent information indicates that a steady state feedwater pH of around 9.8 (as measured at 25 °C) will be needed to minimize the corrosion/FAC to low enough levels to prevent extremely high levels of total iron entering the condensate/feedwater of a plant, and subsequently leading to serious boiler and HRSG tube failures. Most often, plants operate with condensate filters to assist in the removal of the total iron particulate: a 5 µm absolute condensate filter or a pre-filter prior to a condensate polisher provides the best control to minimize the transported iron. There is an ACC Corrosion Index (DHACI) [36] which has been applied to ACCs worldwide so that a unifying indicator can allow qualitative comparisons before and after a change in chemistry control. Plants with major corrosion and FAC at the ACC tube entries in the upper ducting (streets) with DHACI in the range 3 – 5 can expect corrosion product decay profiles in the red area of Figure 9. Also, these damaged areas will corrode further during shutdown periods and result in large levels of CPs in the condensate of these plants. Because of the enormous surface areas in ACCs they are difficult to protect when shutdown.

There are now an increasing number of reports on the experiences of applying FFS in water/steam cycles equipped with ACC [30]. Furthermore, some good results have been presented at the ACC User Group (ACCUG) meetings (<http://acc-usersgroup.org/>), but often when FFS have been added to units with ACCs, there has been no baseline comprehensive monitoring of total iron or inspections of the ACC tube entries using the DHACI [36] so this has not allowed a comprehensive assessment of the improvement after treatment. Plants using an FFS can expect a low DHACI between 1 – 2.

For units with ACC, IAPWS suggests that the sampling and monitoring according to the proxy method (Section 7) are applied at the condensate pump discharge sampling location as well as at the economizer inlet for conventional plants and at the feedpump discharge for HRSGs.

Without the factors above being applied for units with ACC a typical total iron corrosion product decay curve will typically be in the red area on Figure 9 based on actual data from many frequently started units worldwide. Such elevated profiles can be interpreted for these units mainly from the chemistry during operation [36].

9.4 Units using FFS

As discussed in Section 9.5, there is a major difference between power plants in cycling and two-shifting operation, and those with continuous operational periods interspersed with long shutdown periods that might last for months. Cycling operation is often characterized by short operation times with starts and stops daily, mostly unscheduled and often with short notice. Often the duration of the shutdown periods cannot be predicted. Section 8 has indicated that the possibly lowest corrosion product decay curves (within the green area of Figure 9) are achieved by the use of a FFS during operation to protect the oxide surfaces in water-touched areas with the documented results of lower corrosion product transport. For these power plants, a continuous

injection of FFS during operation is preferable because of the short time of operation. Depending on the chosen FFS, the injection can be made in addition to the normal cycle chemistry or as a substitute to the conventional chemicals. Plants using FFS may see an increase in CPT when the application is started due to the mobilising effect on loosely bound deposits. However, CPT at plants using a FFS should expect to see a decrease in CPT over time for comparable operating and shutdown periods as surfaces around the water-steam cycle are progressively conditioned.

Power plants with longer shutdown periods, which need to be able to return to service within a short time period, should increase the FFS dosage prior to shutdown so that a higher concentration of FFS can be measured in the water. During the shutdown period, the water should be recirculated.

9.5 Variability of Shutdown Durations and Speed of Return to Service

(**Note: the STG considers this an important factor for CPs and CPT. It will be further developed as more plants are monitored using the proxy methods)

Historically, unit starts have been described only by the length of the shutdown periods with little thought having been given to the operational chemistry and shutdown conditions. The international community is familiar with hot, warm and cold starts which have loosely been defined as overnight, over an extended weekend (or 3-4 days) and more than five days respectively. In the changing international economic and fuel supply situations in numerous countries worldwide, many combined cycle units are now required to rapidly startup and/or are cycled frequently (such as daily or twice daily start / stop). Sometimes 2x1 or 3x1 combined cycle/HRSG plants are operated in the 1x1 mode with the other HRSGs in the shutdown mode requiring protection. Conventional plants are also being required to start more frequently as well as the complete opposite of being shut down for extended periods (weeks, months). While these operational regimes do not necessitate a change of the normal or target IAPWS guideline limits provided in the operating chemistry TGD [4, 5], there are a number of aspects that operators of currently operating units need to consider to minimize the level and decay of corrosion products to maintain decay levels in the Green area of Figure 9. Experience of IAPWS members internationally is that these types of operating regimes increase the level of corrosion products and extend the periods of elevated decay curves. In turn, the rate of internal oxide deposits in boiler waterwalls and HRSG HP evaporators is widely recognised to increase with cycling operation.

Owners of future combined cycle units where fast start requirements are anticipated should consider incorporating features suggested by IAPWS for cycle chemistry monitoring and control into the initial specifications or later plant modifications [34]. Some of these are at the cutting edge of conventional and combined cycle / HRSG plant technology and, as such, have not become standard practice or had much operational experience.

Very often the duration of the shutdown period is not known and cannot be predicted. For these power plants, a continuous injection of FFS during operation may be preferable [30]. Depending on the chosen FFS, the injection can be made in addition to the normal water chemistry or as a substitute to the conventional chemicals. Power plants with longer shutdown periods, which need to be able to return to service quickly, can increase the dosage prior to shutdown so that a higher concentration of FFS can be measured in the water [30].

The following points represent the consensus experience of the IAPWS Power Cycle Chemistry (PCC) Working Group on factors that can affect and influence both the increased levels of corrosion product generation and their decay during startup periods.

- The operators of these units should try to maintain the positive aspects described in Sections 8.4.1 to 8.4.3, and 9.1 to 9.3.
- Improving appropriate shutdown/layup chemistries as described previously. Improvements should be made by using the proxy methods for corrosion products on each return to service and comparing the decay profiles with the IAPWS Map and with previous profiles.
- The IAPWS Instrumentation Technical Guidance Document has been amended to cover additional instrumentation and sampling requirements for frequently cycled and fast start HRSGs [3].
- 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 [31] during all expected modes of operation with changing temperature profiles should be assessed and inspected.
- It is always most important to identify a condenser leak and distinguish contamination from air in-leakage (carbon dioxide) during a startup [31]. The recently amended IAPWS TGD on Instrumentation [3] suggests that DCACE should be added as a fundamental instrument in superheated steam and at the condensate pump discharge to provide additional guidance for fast start HRSGs.
- For fast start units with an ACC, there is added importance of having a condensate filter to ensure that large amounts of iron do not transport to the HP evaporator of the HRSG during the frequent starts / stops. Experience indicates that a 5 µm absolute condensate filter will keep the total iron in the condensate consistently less than 10 µg/kg.
- In terms of sampling for guideline parameters and corrosion products, locating sampling systems close to the sample origin will be required to procure reliable analytical results.
- The pH should be within startup limits prior to or very quickly after the startup. Consideration should be given to automating the dosing control, where practical, to minimize the duration of chemical excursions and the need for operator intervention during startups.
- The duration of the shutdown periods becomes important on fast start units and operators of plants need to be as flexible as possible due to changing situations where short shutdown periods can change to longer shutdown periods, and vice versa. Many plants may start only by demand of the system/grid and less as a routine plan. Consequently, adequate layup procedures should be adopted to cover shutdowns of greater than 24 hours because, on further unprotected shutdowns, corrosion can quickly become a serious issue.
- Makeup water that is added to water-steam cycle during shutdown periods (e.g. to replace water used for drum level topping up to assist in maintaining return to service times) should be de-oxygenated or appropriately chemical conditioned so that appropriate shutdown conditions are maintained.
- The ability to circulate water circuits periodically during shutdown periods will be of significant advantage to prevent localised corrosion cells becoming established irrespective of chemical conditions.

10. Appendix on Data Processing - the Log-Normal Distribution and Particle Size Distribution

During the research work [11] for this White Paper (pre-TGD), the need for a change in the treatment and reporting of CP data has become obvious. So far, it has implicitly been assumed that CP data followed the normal distribution as most other experimental data, and this has influenced the aggregation and reporting of results and not least the way deviating results were handled. It turns out that the log-normal distribution matches the data observed both in the short- and long- term much better. This relates back to the PSD of the CPs in the sample – when the particle size follows a log-normal distribution, this leads to log-normally distributed analysis results for grab samples. This means that the statistical figures, median value and 95th percentile, should be used to characterize aggregated CP results. These figures are easy to understand and communicate, so this is not a major change. Most importantly, assuming the log-normal distribution sheds bright light over the occasional high results that has so far been taken for outliers and in most cases discarded as such. These results are an integral part of the CP data and throwing them away may give misleading low aggregate values for the CP level in a given sample point. These occasional high results have been associated with sampling system uncertainty or single, large particles in the sample. However, this is not the case; under correct sampling conditions, the sampling system does not occasionally give deviating samples, nor do single particles occur that are large enough to make the total concentration fall out.

10.1 The Log-Normal Distribution

The log-normal distribution implies that the data are normally distributed on the log-axis, i.e. the log-transformed data follow the normal distribution. Figures 11 and 12 illustrate what that means in practice.

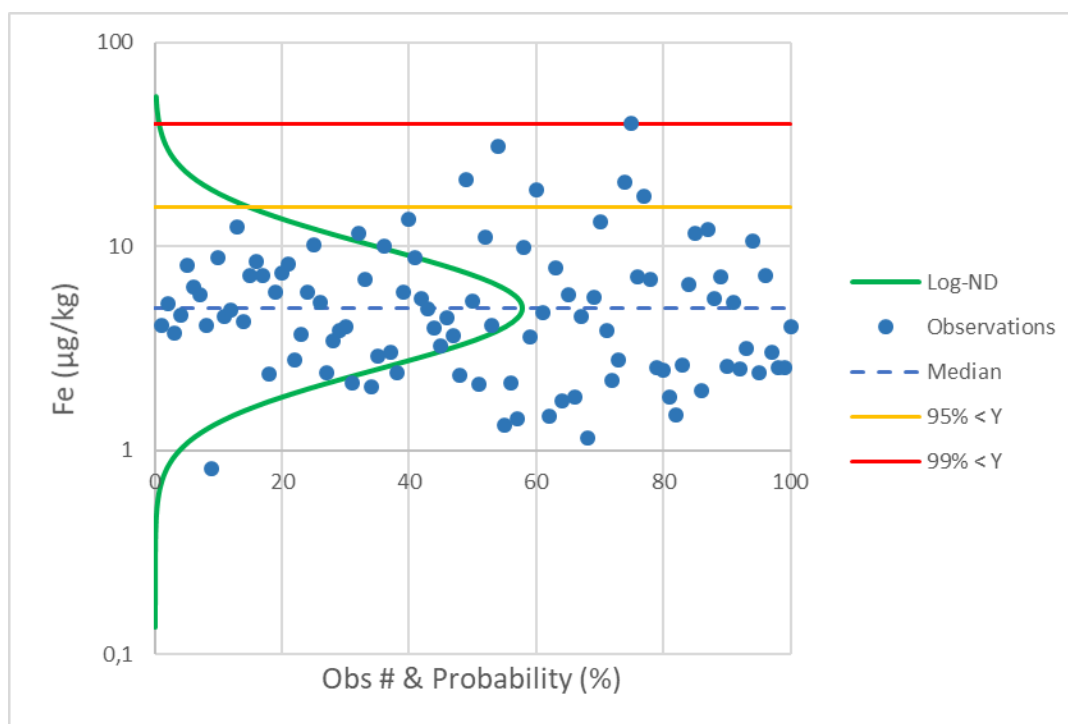


Figure 11. Model data set with 100 results drawn from the distribution depicted on the y-axis. This distribution is normal on the logarithmic y-axis.

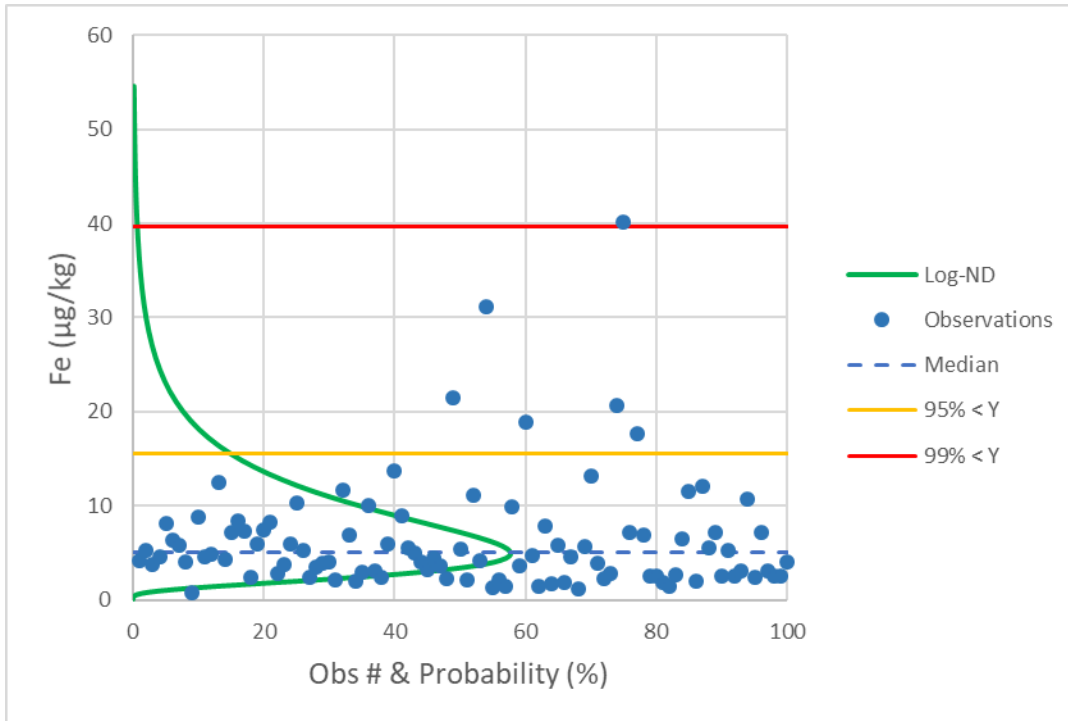


Figure 12. The same data set as in Figure 10 displayed on the ordinary y-axis. Note, how the transformation to the physical scale makes the distribution skew with a long upward tail.

On the logarithmic axis (Figure 11) the distribution is symmetrical with equally many points on either side of the mean. 95 and 99 % of the points fall below the limits marked "95 % < Y" and "99 % < Y", respectively; these mark the 95th and 99th percentile values. On the physical (ordinary) y-axis (Figure 12) the distribution is unsymmetrical with a long upward tail. This means that a fraction of the results will come out markedly higher than the bulk of results around the median value. In the example 6 points are above the 95th percentile and 1 point is above the 99th percentile. This illustrates that from a statistical point of view, 5 observations in 100 and 1 observation in 100 are expected to come out larger than the 95th and 99th percentile, respectively. The median and 95th percentile are convenient figures to characterize an aggregated data set of CPs. Equally many results fall below and above the median, and only 5 % (1 in 20 observations) is expected to be above the 95th percentile. The median value describes the center of the data, and the 95th percentile is a measure of the spread of data corresponding to the usual average and standard deviation figures. Plotting sequential analysis results on a trend curve with the median and 95th percentile values marked (as in Figure 8) makes it conceptually very simple to check if the distribution is stable: In that case, the results distribute evenly below and above the median and only 1 in 20 exceeds the 95th percentile. Clear deviations from this pattern indicate that the distribution has shifted, most likely due to a change in corrosive conditions of the circuit under observation.

10.2 Data Processing and Reporting

The median and 95th percentile values are the simple and straightforward descriptors of a set of CP results, and the values may easily be calculated by the built-in functions of commonly used spreadsheet or statistical software programs. Often, it is of value to get a more complete view of the distribution of observed data, and a plot of the cumulated fraction versus concentration is one way to do that. Here, the data set is ranked according to value, and the cumulated fraction of each point is calculated as:

$$CF = \frac{Rank}{n + \frac{1}{2}}$$

Rank is the position of the given result in the sorted data set, and n is the total number of results.

Plotting the CF versus the concentration on a logarithmic x-axis gives a smooth S-shaped curve, if the data are distributed according to the log-normal distribution. Figure 13 displays an example of data for iron in feedwater measured over a couple of years, and the lines show how to estimate the 95th percentile from the plot. The median is found correspondingly by reading the concentration on the x-axis corresponding to a CF of 50 %.

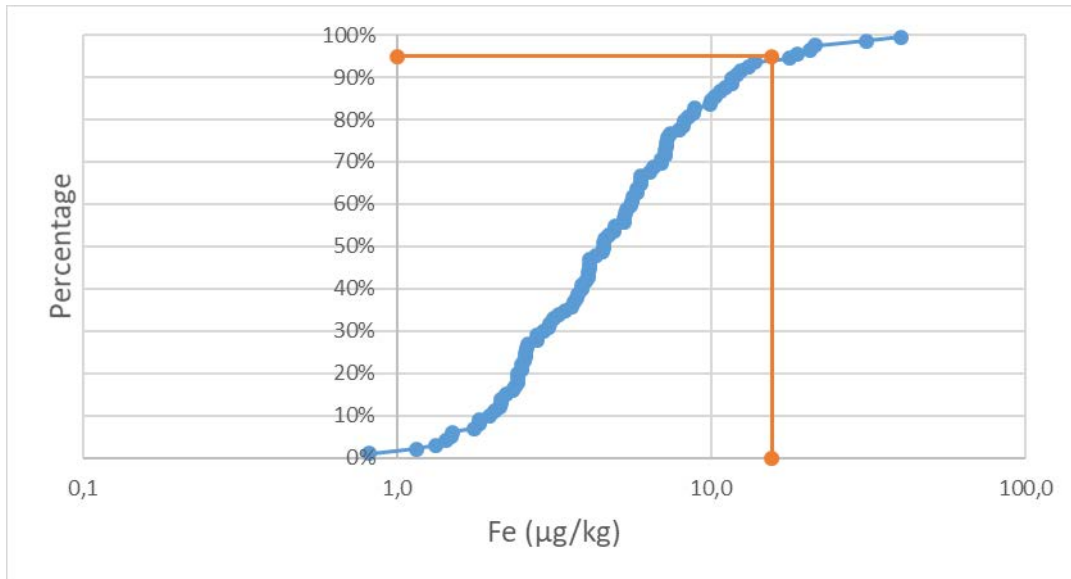


Figure 13. Example of a distribution plot of cumulated fraction versus CP concentration. This data set covers results aggregated through at couple of years routine measurements of iron in feedwater. The 95th percentile is read by finding the value on the x-axis corresponding to a CF of 95 %. Correspondingly, the median value is found on the x-axis as the value corresponding to a CF of 50 %.

The average and standard deviation of the log-transformed data are the best estimates of the true mean (μ) and standard deviation (σ) defining the normal distribution on the transformed scale. Applying these estimates with the built-in normal distribution function of the common spreadsheet or statistical software programs, the model cumulated distribution may be calculated and plotted together with the experimental distribution^a. Figure 14 illustrates this for two sets of iron results aggregated over two three-year periods for iron in feedwater of a drum unit on AVT(O).

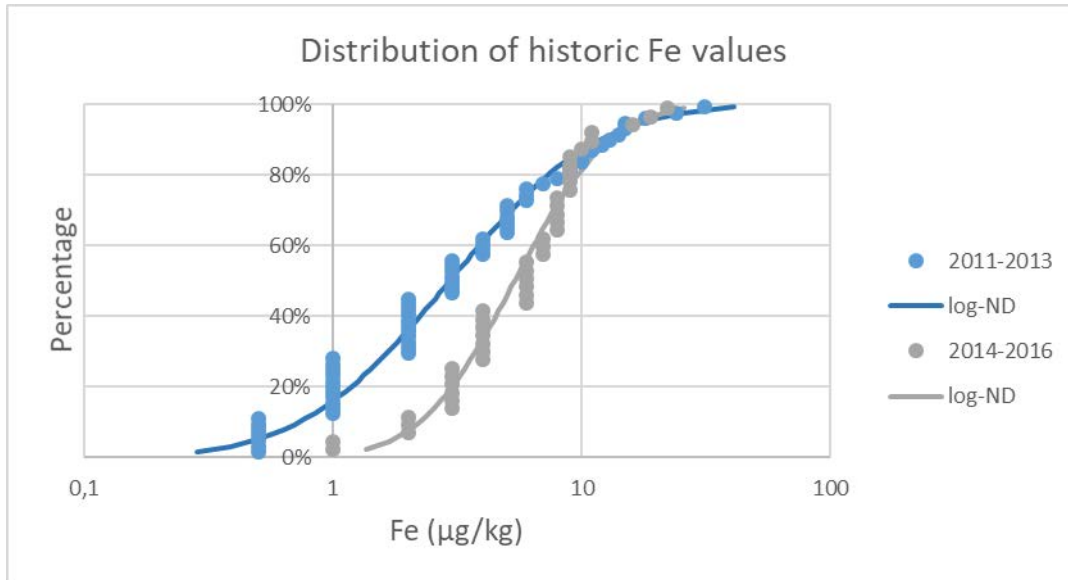


Figure 14. Aggregated iron in feedwater results for two three-year periods plotted with the model cumulated distributions. The model distributions were found by use of the average and standard deviation values for the log-transformed data sets.

The figure shows that aggregated data sets over long periods fit nicely to the log-normal distribution. There is a clear change in distribution between the two periods, the median value increases from 3 µg/kg to 5 µg/kg, i.e. 60-70 % higher CP transport towards the boiler. Most likely, this was a consequence of a change in operational mode, as there was a marked shift from continuous operation with shifting load towards more frequent stops, short outages and even more cyclic load from 2011-2013 to 2014-2016. The shift in level of CPs is much clearer when the data is presented as distributions plots compared to trend curves (as Figure 12) as the random spread of data makes the change subtler to recognize.

10.3 Advanced Use and Tests

The probit plot is another method to test if a given data set adheres to a distribution, in this case the log-normal distribution⁴. The expected result based on the model distribution and the experimental value of CF for each data point is calculated. The observed results are then plotted against the expected outcome from the model distribution. If the two data set match closely, i.e. lie close to the $y = x$ line in the plot, the assumption of a log-normal distribution is acceptable. Figure 15 and 16 give an example. The iron in feedwater for a combined cycle/HRSG plant on AVT(O) was measured by use of the "20 samples in 20 minutes" procedure^[11], i.e. rapid sampling in sequence to investigate the distribution of CPs under approximately constant operating conditions (in this case 5-6 h after startup and steady load). The samples were taken as 1 L samples and filtrated afterwards to determine filtered iron as analytical result. Applying the filtered iron method allowed the laboratory to analyze samples with very low contents of iron. All results were far below the 5 µg/kg quantification limit ordinarily applied.

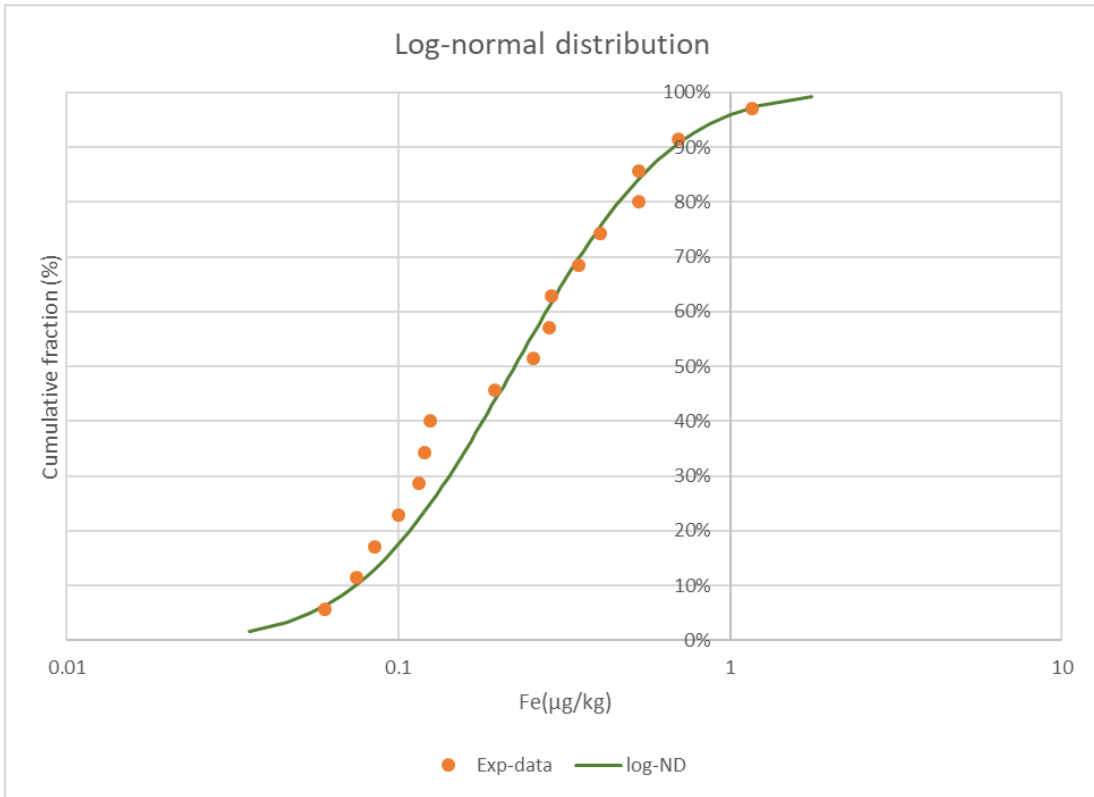


Figure 15. Cumulated distribution of 20 samples taken in rapid succession of feedwater of an HRSG operating on AVT(O). Filtered iron is measured allowing quantification at very low iron levels.

The filtered iron results fit the model curve calculated from the average and standard deviation of the log-transformed data quite well. Next, the expected outcome (iron concentration) from the model for each of the observed CF values is calculated, and the experimental values are plotted versus the model values.

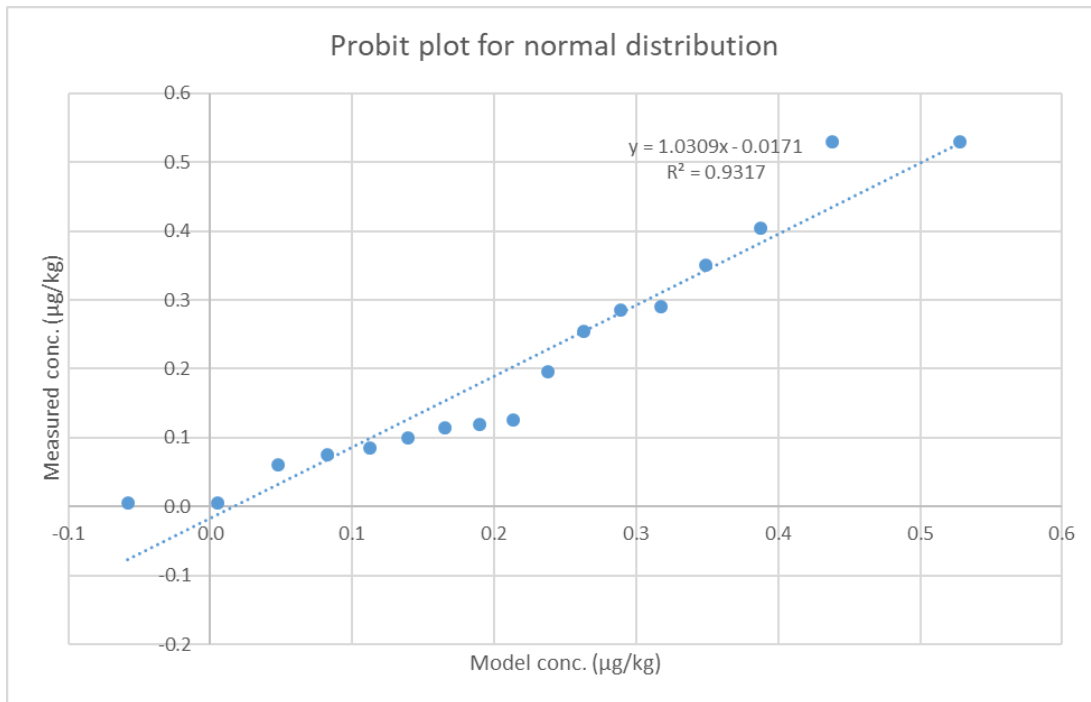


Figure 16. Probit plot, in which the experimental results are plotted versus the model values from the model distribution and the observed CF values.

The relation between the experimental and mode concentrations is close to the ideal $y = x$ relation indicating that the log-normal distribution describes the observed data well. Thus, it may be considered valid to use values derived from this distribution as guiding values for future CP measurements, for instance as median and 95th percentile guiding lines in easy-to-grasp trend curves.

Working on the log-transformed data all the standard tests for normally distributed data^c may be applied in the usual manner, for example:

- F-test to check, if two data sets from different periods or sample points have the same variance
- t-test to check, if two data sets have the same mean
- t-test to check, if the mean of a data set is less than a given guiding limit (i.e. less than the log value of the limit).

Transforming some of the statistical figures back to the physical (ordinary) scale from the log-transformed is relevant, for instance:

- The average value on the log-scale transforms to the median value on the physical scale
- The 95th and 99th percentiles on the log-scale transform to the corresponding values on the physical scale.

Note, that transforming the standard deviation on the log-scale to the physical scale has no real purpose as the resulting value has no physical meaning. Limits of confidence intervals may be

^c Treated in detail in most textbooks on basic statistical analysis

converted to the physical scale and keep their physical meaning, i.e. 95 % of the results are expected to fall within this interval. However, the percentiles are the more operational and understandable descriptors.

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