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The International Association for the Properties of Water and Steam (IAPWS) Power Cycle Chemistry (PCC) Working Group

White Paper

Corrosion Product Sampling, Monitoring and Analysis for Flexible and Fast Starting Plants

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This White Paper has been released by the International Association for the Properties of Water and Steam (IAPWS) Power Cycle Chemistry (PCC) Working Group. An IAPWS PCC White Paper is intended to be a preliminary technical document collating knowledge on a particular subject to provide a basis for the potential future development of a related Technical Guidance Document. They are not formal IAPWS outputs as such.

Summary

This White Paper considers the sampling and monitoring of total iron and copper corrosion products for flexible and fast starting conventional fossil and combined cycle/HRSG plants. It provides correct sampling conditions and appropriate proxy methods such as turbidity and particle counting/monitors to track metal oxides during steady and transient load, and even during startup.

The White Paper introduces a procedure for quantification of corrosion products that reflect the success or failure of the preservation methods applied during shutdown. The IAPWS Corrosion Product Decay Map grades the outcome of this measurement during startup in a simple and illustrative manner allowing an operator to plot the local results directly against the international experience and to improve the operational and shutdown chemistry in a move towards more optimized conditions in the future.

This IAPWS White Paper Document contains 50 pages, including the cover page.

Further information about this White Paper and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS (Dr. D.G Friend, dg.friend@iapws.org) or from http://www.iapws.org.

Contents

1. Nomenclature and Definitions

Term	Alternative or Acronym	Definition
All-volatile Treatment	AVT AVT(R) AVT(O)	Conditioning regime in which only volatile alkalizing agents are added to the feedwater (commonly ammonia, but other volatile amines may also be employed) May be either: 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 to the condensate pumps
Conductivity	Specific Conductivity Direct Conductivity	Electrical conductivity of the water sample as measured directly without any treatment
Conductivity after cation exchange	CACE Cation Conductivity Acid Conductivity	Conductivity of a water sample after passage through a strongly acidic cation exchanger in the hydrogen form
Caustic Treatment	CT	Involves addition of NaOH to the boiler or HRSG evaporator
Corrosion Products	CP	Corrosion products take the form of particulate and dissolved for both iron- and copper-based materials
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 condensate pumps, the low and high pressure feedwater heaters to the boiler

Term	**Alternative or Acronym**	**Definition**
Filter Iron	Filter-Fe	Iron particles retained on a 0.45 µm filter after filtering a 1 L water sample. The concentration of filter-Fe is determined by digesting the filter and the iron particles producing a solution with dissolved iron. Subsequently, the solution is analysed to determine the iron concentration.
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	µg/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 (TSP) to the boiler water

2. Introduction

IAPWS has previously issued a Technical Guidance Document (TGD6-13) [1] for total iron and copper corrosion product sampling and analysis at plants operating at steady state/base load. In practice, many plants worldwide have flexible operating regimes with frequent load changes and start/stops. For these plants, most corrosion product transport into boilers will occur during these transient periods rather than at steady state, particularly if the chemical conditions during shutdown/layup do not properly prevent corrosion.

This White Paper extends the methodology for the sampling and measurement of corrosion products to startups and transient load conditions using appropriate proxy methods such as turbidity and particle counting for continuous monitoring. The White Paper also introduces the IAPWS Corrosion Product Decay Map as a simple and illustrative way of graduating the amount of corrosion products transported during startups 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. Operators can plot their own plant results directly on the map to compare against international experience and use to improve the operational and shutdown chemistry to move towards more optimized conditions. This will improve the integrity of water-steam cycle components and can also lead to faster startups with a corresponding cost reduction.

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 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 or chemical suppliers guarantees. Adoption of the optimum sampling and analytical processes described may provide levels of corrosion products that are different from those suggested by manufacturers and/or supplies. Each should provide a set of target values representing the plant as designed/operated and these may be slightly different from the operating guidance provided in this document.

3. The Challenge of Corrosion Product Monitoring during Flexible Plant Operation

The IAPWS Technical Guidance Documents for cycle chemistry control [2,3] include suggestions for corrosion product levels 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 (LP and HP). 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 can act as initiating centers for other failure/damage mechanisms such as under-deposit corrosion (UDC) on boiler waterwalls and HRSG evaporator tubing.

The Normal/Target values for chemical monitoring parameters that are promulgated in these documents and customized as needed, consistent with the plant characteristics, are expected to produce the minimum levels of corrosion products. Corrosion product monitoring should be an essential part of cycle chemistry monitoring programs to determine if the chemistry treatments and operating regimes are optimized or need improvement. The existing TGD6-13 [1] on corrosion product sampling and analysis supplements the IAPWS cycle chemistry guidance documents to ensure that corrosion products are monitored using adequate and effective sampling and analytical techniques for monitoring again under steady-state conditions.

In practice, many plants worldwide operate with flexible running regimes that can include frequent load changes, several start/stop events per month or even daily start/stops. For many years, it has been well understood that corrosion product levels are elevated during startup periods and can be significantly above the IAPWS levels for steady-state operation [1], and that often these periods can extend to many hours after startup. As a result, the corrosion product levels in some plants may never reach or decay to the steady-state IAPWS levels. One of the first studies of the decay of iron and copper corrosion products during startups was conducted in the 1970s [4]. Figure 1 shows for very frequently started mixed-metallurgy fossil coal-fired 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 such as shown in Figure 2 [5]. Additional work [6] 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). A further set of results has been observed when film forming substances (FFS) have been added to the plant chemistry [7]. Similarly, the disturbances caused by load changes also result in a short-term increase to corrosion product levels even at plants that are in continuous operation.

For plants with frequent start/stops, the chemical conditions during shutdown/layup significantly influence the transport of corrosion products during operation. Preservation during shutdowns can be an issue, particularly for short standing periods where the optimum preservation measures are often compromised to meet unpredictable generation dispatch. This affects the shutdown chemistry and can allow corrosion to occur 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 chemical cleaning – may be associated with startups and the many load changes during operation.

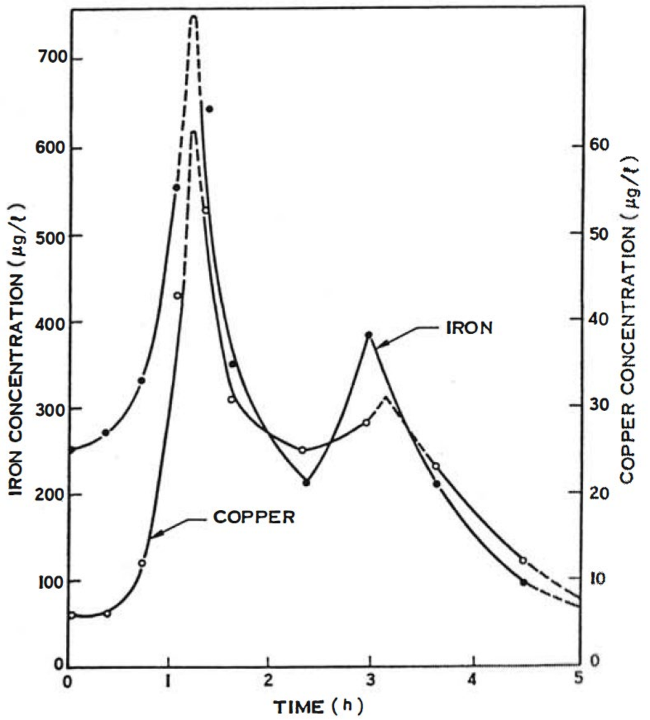

Figure 1. Release of iron and copper oxides following a startup of a mixed-metallurgy unit [4]. The time scale is relative to synchronization in this case.

Figure 9. Feedwater suspended corrosion product content during startup of a 500 MW unit after a 14 hour outage; 100 % condensate polisher

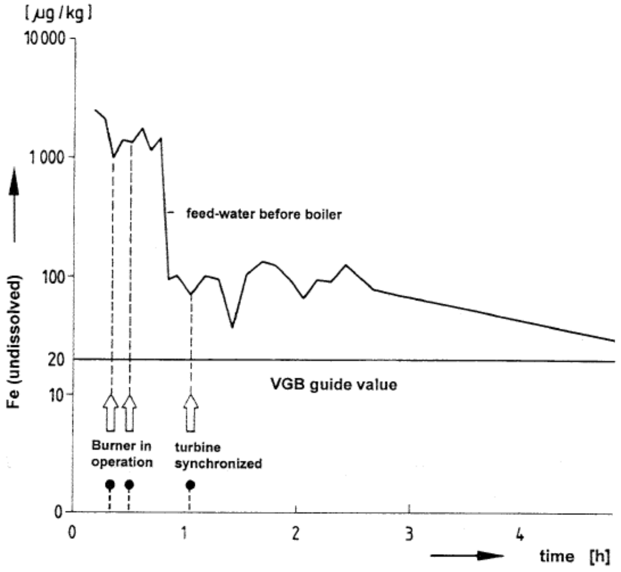

Figure 2. Feedwater suspended corrosion product content during startup of a 500MW unit after a 14 hour outage; 100% condensate polishing [5]

For plants with frequent start/stops and load changes, it follows that simply carrying out corrosion product monitoring at steady state conditions can not only be often difficult to schedule, but most importantly, may be of limited value as the results will not necessarily be representative of startups or operating periods with frequent load changes when most of the corrosion product transport into the boiler actually occurs. Conversely, the challenges for corrosion product monitoring during startups and transient loads are how to measure iron and copper levels under rapidly changing conditions and then understanding what the results mean for the effectiveness of cycle chemistry operational control and shutdown protection, and the associated potential risks to plant integrity and operability.

Consequently, this White Paper has been developed by IAPWS to extend the methodology for the sampling and measurement of corrosion products to startups and transient load conditions. Monitoring these situations requires online 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. The outcome of the proxy methods must have a high correlation with the classical analytical methods for the measurement of corrosion products to relate to existing guiding values under steady-state and also for the transient situations as described in various publications. The filtered iron [8] (or copper) method introduced in this document constitutes the link between the particle-based proxy methods and the reference methods. In the filter method, water samples are filtered through a 0.45 μm membrane filter to collect iron particles. The filter and the iron particles are digested to dissolve the particulate iron and the solution is analysed to determine the iron concentration. Experience [9] gained during the research phase of this White Paper indicates that the filtered iron results correlate well with the responses of the particle based proxy methods. The filtered iron method also improves the sensitivity of detection so that iron concentrations below 2 ppb can still be reliably measured.

The most important application of the methods introduced in this White Paper is the measurement and benchmarking of the iron (and/or copper oxides) transported into the boiler or HRSG evaporator during startups. A key part of the White Paper is the introduction of the IAPWS Corrosion Product Decay Map for operators to use to graduate corrosion product transport during startups and the time necessary to reach corrosion product levels comparable with the guiding value for steady operation. The intention is for operators to plot their own plant results directly on the map to provide a simple visual comparison against international experience. This approach has been used by IAPWS Power Cycle Chemistry Working Group members to assess corrosion product transport at a number of plants.

For plants operating with elevated corrosion product profiles on the decay map, this should be used to prompt action to improve the operational, preservation and shutdown chemistry. Improving the chemical conditions during these phases will be reflected in significantly lower concentrations of corrosion products at subsequent startups. This approach will ultimately benefit plants by improving the integrity of components, plant operability (e.g. avoidance of problems with valve operation and monitoring equipment related to deposited oxides) and can also lead to faster startups.

4. Fundamental Requirements for Corrosion Product Sampling and Analysis

4.1 Existing IAPWS Guidance

The current IAPWS Technical Guidance Document [1] provides definitions, technical descriptions and guidance for corrosion product sampling and analysis for steady state/base load operation plants. This includes guidance on the following aspects:

a) the problems that can exist with the physical sampling of corrosion products in flowing water and steam, how these problems occur and can be avoided.
b) Achievable corrosion product levels for normal operation (at steady-state, full load conditions).
c) an outline of an optimum sampling system for the representative sampling of corrosion products.
d) the various analytical methods that can be used for the analysis of corrosion products with the advantages and disadvantages of each method clearly outlined.

The information provided covers much of the fundamental requirements for effective corrosion product monitoring at flexible operating plants. Hence most of the guidance is not duplicated in this current White Paper and the reader is cross-referenced to the original document. However, some of the basic requirements for corrosion product monitoring that are often still overlooked in plant setups and programs are re-emphasized in this section as they can lead to sub-optimal results and conclusions. Sample point selection for corrosion product monitoring at flexible operating plants is discussed in Section 6.

4.2 Total and Dissolved Corrosion Products

In power plant water-steam cycles, iron and copper corrosion products can circulate in both dissolved (soluble) and particulate (insoluble) states. However, it has been widely recognized for many years that iron is predominantly present in particulate form in all power plant cycles. For copper corrosion products, often a higher fraction is present in dissolved form compared to iron. The fact that iron-based corrosion products are mainly present in particulate form is the reason why proxy measurement methods such as turbidity and particle monitors are viable techniques (the customization of the proxy methods for corrosion product monitoring at plants containing copper alloys is described later in the appendix of this White Paper). Hence it is essential that sampling arrangements and analytical methods are optimally setup for total corrosion product measurement (the sum of particulate and dissolved corrosion product concentrations) to enable representative samples to be delivered and to be able to correctly establish correlations between the results of grab sample analyses and online proxy measurement methods.

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.

4.3 Sample Line Setup

The governing principles and practical realization of sampling systems are covered in detail in TGD6-13 [1]. As part of this, the following two requirements must be recognized for representative corrosion product sampling:

1) Any filters or strainers on the sample lines to on-line particle monitoring instruments and manual grab sampling lines must be bypassed or removed; otherwise, the corrosion product levels that are measured may not be completely representative of actual plant conditions.

2) The flow rate through the sample line and sample coolers must be sufficient to establish turbulent conditions to avoid particle settlement or release within the lines.

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.

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

4.4 Grab Sample Analysis

The chemical analysis of grab samples continues to be the reference method for monitoring corrosion product levels and transport for flexible operating plants. Even when proxy methods are applied for on-line monitoring, the results must be correlated with results of grab samples to interpret them correctly. From the previous discussion, it follows that for any plant, it is essential that chemical analytical methods include a suitable particulate digestion stage for the measurement of total iron or copper corrosion product concentrations. TGD6-13 [1] provides guidance on methods for corrosion product analysis.

5. Introduction to Proxy Methods

Proxy analytical measurements can be used for parameters that cannot be directly measured and quantified if a clear correlation can be properly established. In relation to CP transport in water-steam cycles, proxy methods can be used for on-line monitoring of iron concentration as this has traditionally only been monitored by manual sampling and laboratory analysis. The proxy methods that have been tested for on-line monitoring of CP transport are based on turbidity, particle monitoring and particle counting.

5.1 Turbidity

Turbidity is the reduction of transparency of a liquid caused by the presence of undissolved matter [10]. Water appears increasingly turbid with increasing amounts of suspended matter due to the scattering of light by the oxide 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 of the diffuse radiation depends upon the wavelength of the incident radiation, the measurement angle, and the shape, optical characteristics and particle size distribution of the particles suspended in the water [10].

ISO 7027 specifies that the wavelength of the light source must be 860 nm (infrared light), whereas EPA 180.1 calls for the use of a light source with a wavelength in the range of 400-600 nm (white light) when the turbidity is below 40 NTU (extremely high turbidity for the present application). However, it has been shown [11] that a light source with a wavelength of 860 nm is advantageous when it comes to the detection of black magnetite. All turbidity data in this White Paper has been acquired by turbidity instruments utilizing infrared light (860 nm), and thus, FNU (Formazin Nephelometric Unit) is used as the unit for turbidity as opposed to NTU (Nephelometric Turbidity Unit) for measurements using white light based on EPA 180.1.

Turbidity is an optical property depending on the scattering of light from particles meaning it is not a direct measurement of the particle concentration in the water. Hence, it is referred to as a proxy method. The extent of scattering depends on concentration, colour, size, size distribution and shape of the particles in addition to the refractive index of the solvent. Even ultrapure water will scatter light to a certain degree meaning that no solution can have a turbidity of 0 FNU. With turbidity measurement, particles in the nano-meter range are detected [11]. This is important as in conventional fossil and combined cycle/HRSG plants, particles range in size from a fraction of a micrometer to about 10 µm, with an average size of about 1 µm. For CP monitoring, particle colour plays a crucial role as the black magnetite absorbs more light than the red hematite leading to the turbidity response of hematite being about three times greater than that of magnetite [11] [12].

The considerations above demonstrate that turbidity is not a completely accurate measurement of CP concentration in the relevant sample streams. Thus, on-line monitoring of turbidity can only be considered as a semi-quantitative technique to establish the CP levels and transport. Figure 3 displays the correlation between filter-Fe and turbidity for samples from several different plant types, feedwater chemistries (all oxidizing) and sampling points.

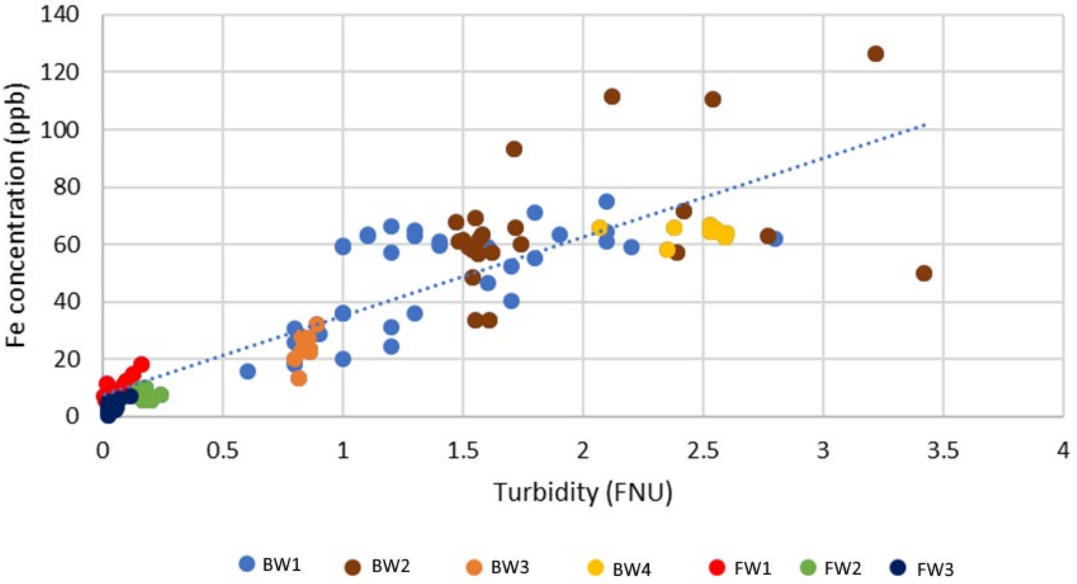

Figure 3. Correlation between filter-Fe and turbidity under different conditions with respect to plant type (once-through combined cycle/HRSG), feedwater chemistry (AVT(O), AVT(O)+FFA, and OT), and sampling point (boiler water and feedwater). The data points below 0.5 FNU represent feedwater samples whereas the data points above 0.5 FNU represent the boiler water samples [14].

Figure 4 displays an example of the correlation between filter-Fe and turbidity for a specific plant and sampling point.

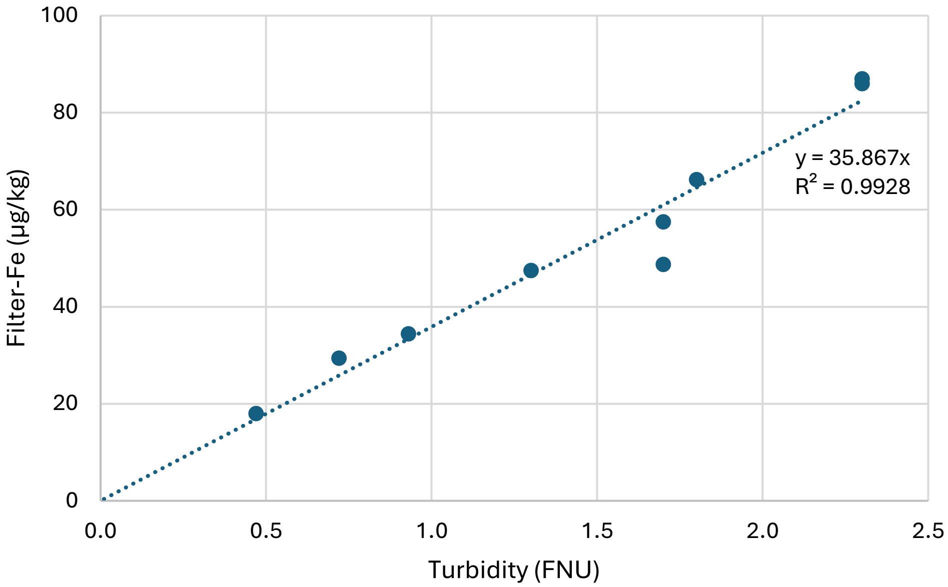

Figure 4. Correlation between filter-Fe and turbidity in feedwater during a startup of a combined cycle/HRSG plant [14].

As the correlation factor between turbidity and iron concentration depends on many variables, the correlation factor will vary for different plants and sampling points. Thus, the correlation factor should be established based on measurements for individual plants and sampling points. Ideally measurement campaigns should be repeated to acquire a representative date set.

5.2 Particle Monitors and Particle Counters

Particle monitoring is a technique that gives the number of particles per volume, and particle counting is 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).

Some particle monitors and particle counters rely on the shadowing effect of a particle passing an illuminated optical sensor. The light from an 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 result is given as number of particles per time/volume. The height of the pulse may by calibrated to the particle size by use of particle size standards with well-defined particle sizes. In this way, particle counters give both a total count per time/volume and the PSD as output.

For optimum 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. As described previously, the average size of iron oxide particles in power plant water-steam cycles is approximately 1 µm such that instruments limited to particle sizes above this will misjudge the total number of particles present. An example of a field study of feedwater particle distribution can be found in [9] for both steady load and transient conditions.

Particle monitors are subject to limitations regarding the correlation between number of particles and iron concentration because the particle size is not considered. The concentration of iron is proportional to the median particle diameter in the third power meaning that a slight increase in the particle diameter will lead to a large increase in the concentration. Typically, the median particle size increases under transient load conditions [8,9] meaning that particle monitoring is limited as a proxy method for iron concentration under flexible operating conditions because the correlation with particle concentration is likely to underestimate the iron concentration. As with turbidity, only a semi-quantitative correlation between the iron concentration and the number of particles may be established.

Particle counters that register the PSD can to some extent accommodate this as the median diameter may be calculated for each measurement. Thus, the influence of varying particle size with operating conditions can be considered when comparing with results of iron concentration. The key point here is that the particle size interval evaluated should match the particle size distribution of the sample though recognizing that the correlation will have some limitations due to the influence of particle shape on particle size distributions and consequently the median diameter that is calculated. With knowledge of the particle size and some basic assumptions on chemical composition and porosity of the CPs, this allows again semi-quantitative calculation of the CP concentration. As an example, the iron concentration may be estimated by the equation:

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

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

5.3 Correlation between Proxy Methods and Iron Concentration

As described, turbidity is a function of the number of particles present, size, size distribution, shape and also particle color amongst other variables. Parallel measurements of turbidity and particle number/PSD show some of the potential limitations of turbidity as a proxy method [9].

Hence turbidity can only be used as a semi-quantitative method (as with other proxy methods) and requires a thorough calibration stage to establish a satisfactory correlation with iron concentration.

Figure 5 shows the correlation between turbidity and number of particles per volume during a transient load situation for a once-through boiler on OT. The correlation appears linear up to about $2 \cdot 10^6$ particles/L after which it gradually shifts to a quadratic relation, which it is assumed is most likely from secondary scattering effects as the number of particles increases.

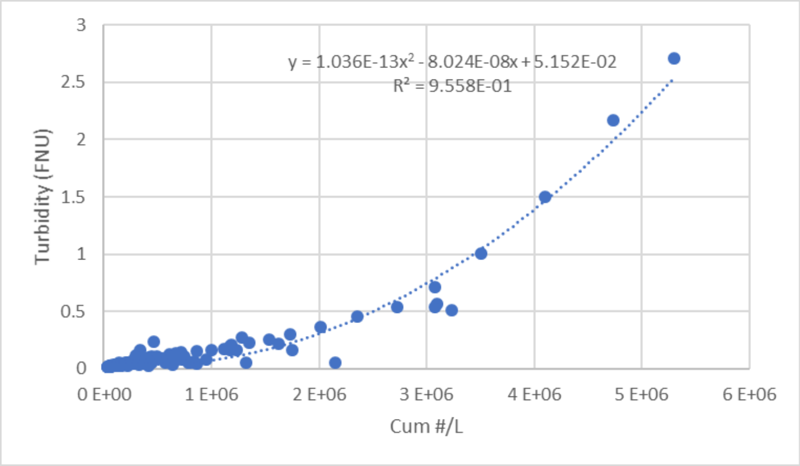

Figure 5. Correlation between turbidity and number of particles per volume. The measurements were conducted in feedwater for a once-through fossil boiler operation on OT during a load increase from 30 to 60% in the course of a time period of 10 minutes [9].

Figure 6 shows the correlation between turbidity and mean particle diameter for the same dataset [9]. By knowing the number of particles per volume and the PSD, the iron concentration can be calculated from the equation above. By dividing the turbidity with the calculated iron concentration, the turbidity is standardized to show how the mean particle diameter influences turbidity. The results of this can be seen in Figure 6.

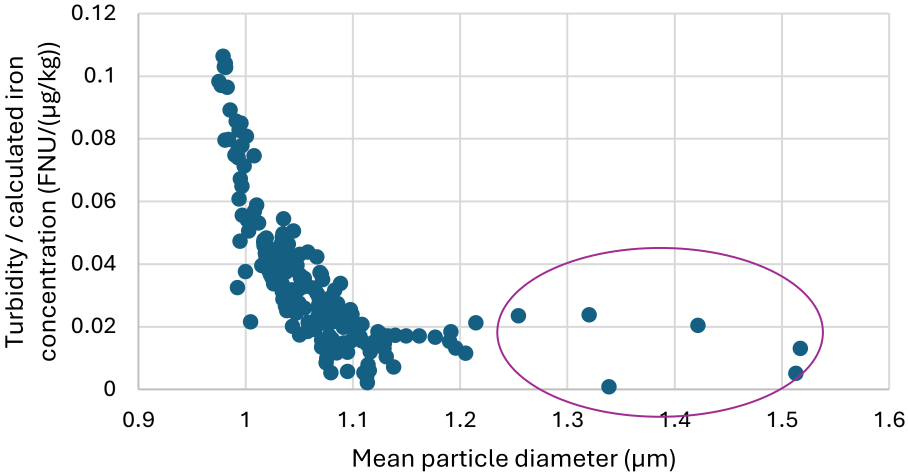

Figure 6. The ratio between turbidity and calculated iron concentration plotted against the mean particle diameter. The measurements were conducted in feedwater for a once-through fossil boiler operation on OT during a load increase from 30 to 60% in the course of a time period of 10 minutes. The circled data represents the peak of the load increase with iron concentrations above ~50 µg/kg [9].

Figure 6 illustrates how turbidity depends on particle size. This shows that smaller particles result in a higher turbidity. The reasoning for this is the effect of Mie scattering. This means that a large number of small particles will give a very high turbidity value, whereas a few large particles will give a low turbidity value, but in reality, the two samples could contain the same iron concentration.

In Figure 6, the data points circled are from a transient event. During transient events, the mean particle diameter increases, but it can be seen in Figure 6 that the turbidity plateaus when the mean particle diameter reaches a certain point. At transient events when there will typically be more particles with a larger diameter present, this means that the turbidity will underestimate the effect of the large particles and thus the iron concentration.

Hence turbidity can only be used as a semi-quantitative method and requires a thorough calibration stage to establish a satisfactory correlation with iron concentration.

6. Sample Point Selection

With the procedures introduced in this White Paper, there are two basically different rationales behind corrosion product analyses:

1) The standard approaches described in TGD6-13 [1] take samples from various locations in the water circuits under well defined, steady-state and high load conditions to be able to compare results between campaigns and with the IAPWS guidance. To provide satisfactory indication of plant condition, a number of sampling locations are recommended dependent on plant and cycle design. The purpose of this is for plant operators to use to optimize and customize the feedwater chemistry of supercritical units and combined cycle/HRSG plants and the boiler water chemistry in units with drum-type evaporators. In TGD6-13, a summary table is provided of key corrosion product sampling locations for plant operating under steady state conditions.

2) In this White Paper, the procedures and methods outlined instead focus on the measurement of corrosion products and other oxides during transient load and startup situations. The purpose of such measurements is to characterize the transport of corrosion products (and other oxides) that are carried forward from the condensate and feedwater systems into the boiler/HRSG. This should be used by operators to prompt and assess changes in procedures (e.g. for operation, preservation and startup) for the reasons described in Section 2 about potential plant impacts.

Therefore, the recommended sampling point for monitoring corrosion product transport during startup and transient load conditions is the **economizer inlet** in order to measure the amount of corrosion products in the feedwater before supply to the boiler/HRSG. In practice, the sampling location of interest needs to be a sampling point before the boiler/HP evaporator and as close to the boiler as possible. If the power plant has an economizer before the boiler, and there is a feedwater sampling point before the economizer, this is the proper sampling point. For HRSG plants, the equivalent location is at the boiler feedpump (HP/IP economizer inlet).

In HRSGs where the LP drum also acts as a deaerator / feedwater storage tank for the higher pressure IP and/or HP circuits, the preferred sample point for monitoring corrosion product transport during startup and transient load conditions remains the boiler feedpump (HP/IP economizer inlet) downstream of the LP drum (i.e. not condensate or LP economizer inlet sample points).

In drum-type boilers, the same approach for continuous corrosion product monitoring that is outlined in this White Paper can also be applied to the monitoring of boiler water samples to enhance corrosion product monitoring programs compared to only grab sampling routines, particularly where these are used to provide an indication of flow-accelerated corrosion (FAC) in HRSG feedwater and evaporator circuits. In these cases, a specific correlation between iron levels and proxy instrument readings needs to be established for the boiler water sample; correlations from other sample points cannot be simply transferred because the type and size distribution of corrosion product particles may be different which would result in a different response from the proxy measurement instrument.

It should also be noted that the IAPWS Decay Map presented in this White Paper (Section 7) only applies to feedwater monitoring and at this time there is no equivalent map for corrosion products in boiler water samples from fossil and HRSG drum-type units. This should not preclude an operator from making their own studies using boiler water samples and comparing performance before and after any improvements in order to achieve plant-specific program objectives.

7. Introduction to the IAPWS Corrosion Product Decay Map

The previous sections of this document have described the background to the approach for sampling and monitoring by proxy methods for iron (and copper) in frequently started and fast starting conventional and combined cycle/HRSG plants. A typical decay profile is shown later in Section 9. This current section provides operators with an introduction to the IAPWS Corrosion Product Decay Map, how to use it and how to interpret the results in terms of whether the operational and/or shutdown/layup chemistries of the plant are optimized or not.

Some early studies of the decay of iron and copper corrosion products during startups were shown in Figures 1 and 2 in Section 3. These showed for very frequently started all-ferrous and mixed-metallurgy fossil coal-fired 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. Subsequently the same trends have also been demonstrated in many other plants worldwide. These observations have now been developed into the IAPWS Corrosion Product Decay Map [Figure 7] to allow operators to review the results of the proxy analyses such as shown in other sections.

The decay map has been constructed based on: a) two IAPWS International Collaborative Projects involving plant monitoring in Denmark, UK, Australia, New Zealand and USA [8, 9, 14], b) the wide experience of IAPWS members worldwide with internal deposit levels which can result in damage such as under-deposit corrosion (UDC) and overheating [15], and c) literature on monitoring corrosion products in cycling plants [6, 16,]. Figure 7 is the standard base decay map which can be used by operators and chemists worldwide. Figure 12 (in Section 9) shows an example where a decay profile has been overlaid indicating a well operated unit with the profile in the green area of the Decay Map.

The Map allows iron and copper corrosion product decay profiles to be overlaid.

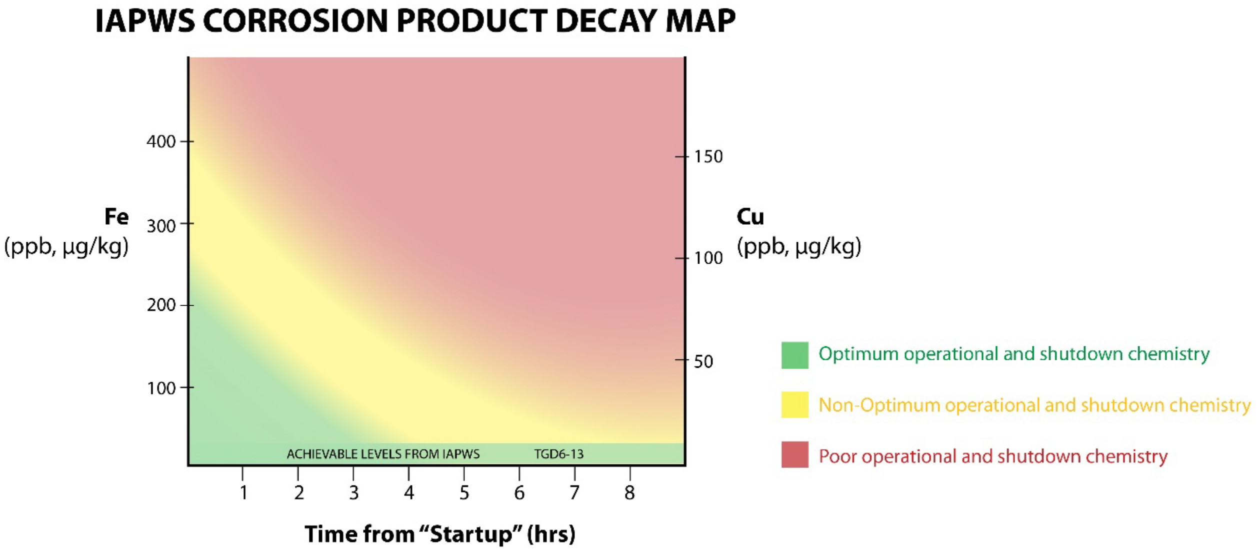

Figure 7. The IAPWS Corrosion Product Decay Map.

A few notes of guidance can be identified:

i) The area under a decay curve represents 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 decay curve (elevated level of corrosion products) on return to service but also the length of time that there is elevation are both most important. The higher an organization's profile relates to the IAPWS Decay Map, the worse is the operational chemistry and/or shutdown/layup shutdown conditions. A review of the factors in Section 10 will direct the operator to possible improvements in both.

ii) The green area on the map (lower left) should be the goal for plants when operating and shutting down units optimally. Monitored levels above these should trigger work to improve both factors.

iii) Profiles in the yellow or red areas are examples of much poorer operational and/or shutdown chemistries. Quite typically for poorly operated plants the decay profile will be in the yellow or red areas with an overall aim of it reaching the green area shown along the bottom of the Decay Map. Often for these plants it can take 3 – 8 hours after startup as indicated on the Decay Map.

iv) To reduce the risk of heavy deposits and under-deposit corrosion [15, 17, 18] on conventional plant waterwalls and on HRSG HP evaporators, an operator should aim to have the decay profiles from the Fe (and 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, the protection provided during the shutdown and the rate at which a unit is brought back into service and how soon the decay profile reaches/approaches the green area. These are covered under Customization in Section 11.

vi) The time to reach “approximate achievable IAPWS levels” (the green band along the bottom of the decay map) 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 may never reach these levels.

vii) The standard Decay Map shown in Figure 7 requires “the time from startup”. IAPWS considers that zero time represents start of the boiler feed pump(s), but recognizes that operators worldwide might use first fires, synchronization, pressure changes or other operational features. The Decay Map can accommodate these, but IAPWS notes that an operator should maintain this criterion during all monitoring campaigns.

viii) The Map and Section10 should be used to develop lower corrosion product transport rates by changing the operational and/or shutdown/layup chemistry to more optimum by application of the guidance in Section 10.

ix) Because each unit monitored is different in terms of equipment, surface area, operating and shutdown/layup chemistry, it is emphasized that while there are coloured areas on the IAPWS Decay Map, the operator/chemist should be more interested in the reasons that plants can achieve the lowest corrosion product transport levels or concerned why the monitored decay profile shows severely high transport levels.

8. Sampling and On-Line Monitoring of Corrosion Product Transport

This section describes the procedure for grab sampling and on-line monitoring of CP transport during transient load conditions. The method described focuses on the on-line monitoring of turbidity and parallel grab sampling for the quantification of particulate iron (filter-Fe). Hence, it is also described how to filter the grab samples to obtain filters that are ready for analysis. In practice, other proxy methods can be used as well as turbidity (i.e. particle counters and monitors) if the selected instrument is suitable for the expected particle size range. There are also different analytical methods that can be used to determine the concentration of CPs in grab samples which are described in Table 6 in TGD6-13 [1].

8.1 Definition of Start Time for the IAPWS Decay Map

In practice there is no clear definition of a startup of a power plant that can be applied to all plants and this needs to be decided locally by the operator. As a general principle, a specific standard operating event should be chosen that can be used to clearly and reproducibly mark the start of any monitoring campaign.

For unit startups, the following events may be used as the starting point for measurements:

- Start of boiler feed pumps or start of feedwater forwarding to the boiler/HP evaporator (if the feedwater is initially recirculated around the boiler feed pump for an extended period). Monitoring from this time captures the initial flux of corrosion products that may be missed from later starting events as a result of system flushing.
- Start of fuel feeding or burner in operation (coal or biomass units).
- Steam flow increase above zero / start of unit operation with the steam turbine in bypass.
- Steam admission to the turbine / start of turbine run-up.

- Steam turbine / generator synchronization.

For plants that do not have frequent startups but instead follow a load cycling regime, there might not even be a startup but just fluctuations in load. Thus, the definition for a startup is specific to individual plants.

For the purpose of CP monitoring presented from here on, startup refers to the start of the measurement campaign.

For the use of the IAPWS Decay Map for evaluation of CP transport, the startup time (time = 0 h) must be chosen for each individual plant so all CP transport is captured during the measurement campaign. In practice, this means that it is better to start the measurement campaign a little too early to make sure no CP transport is missed, and then the startup time can later be set to the time of the event leading to the first spike of CP transport. For multiple repeated measurement campaigns, it is important to choose the same startup time to be able to compare the CP transport.

The measurement campaign is over when the turbine has been synchronized and the unit is operating at steady load. In "dirty boilers", CPs may continue to circulate several hours after this and, in these cases, data acquisition should be continued until CP levels have decayed to near normal values (which may take several hours). This can be evaluated by proxy measurements or by the decreasing colour intensity of filter stains if grab samples are filtered in parallel.

8.2 Sample Flow and Sample Line Requirements for On-Line Proxy Instruments

The demands for turbulent sample flow to obtain representative CP samples are contradictory to the specification of the proxy methods that require a steady, low flow to the measuring cell. Where the turbulent flow conditions call for a flow rate of typically 2-3 L/min, most proxy method instruments demand steady flow rates between 0.05-1 L/min. It must be stated that flow rates of 2-3 L/min represent the ideal sampling conditions, but those conditions are rarely met during startups.

In the beginning of startups where most iron is being transported, turbulent flow conditions are rarely met. Flow rates of around 1.1-1.3 L/min are in most cases achievable during the initial stages of a startup but it depends on the power plant. The flow rate should not be changed during sampling and on-line monitoring so in most cases the flow rate should be set to and maintained at around 1 L/min during the period of sampling and on-line monitoring.

As described in TGD6-13 [1], for sampling systems that are already constructed and in service, the highest linear flow velocity that can be sustained should be imposed. This maximum flow rate is often limited by the capacity of the sample cooler and the maximum allowable sample temperature prior to the online analyzers. Most commercially available sample coolers have a maximum capacity of about 1 L/min. Increased capacity sample coolers may need to be installed in some systems to enable high flow velocities for turbulent sample flow to a proxy analyzer if there is also closed cooling water system capacity available and space for installation.

The challenge regarding the different flow requirements for sampling and the proxy methods is solved by fitting a constant head device or back-pressure relief valve to the sample line before the proxy instrument. Both are valves that split the sample flow into a sample stream to the instrument and a bypass stream to the drain. The valves maintain a constant, adjustable pressure on the instrument inlet, and thus the optimal steady flow for the monitor may easily be tuned in. When the pressure in the sample line varies, e.g. due to load variation, the valves divert more or less of the main sample stream to the bypass maintaining the steady flow to the instrument.

The use of a constant head device in the sample line set-up is critical for obtaining representative CP monitoring data. When measuring turbidity, measurements will change if the flow to the instrument changes, which can lead to incorrect determinations of actual corrosion product levels. It is strongly suggested that the turbidity analyzer has integrated a sample flowmeter with alarm for turbidity measurement validation. Experience has shown that omitting constant head devices and lack of flow regulation to proxy instruments will result in poor correlations being derived between turbidity and CP levels.

8.3 Set-Up for On-Line Monitoring Instruments

On-line monitoring is done by means of proxy methods – either by measuring turbidity or particle counting/sizing. In this guidance, turbidity measurement is mainly described, but many of the same principles apply to other proxy methods.

The turbidity meter must be able to measure continuously during the startup once the flow of water to the sensor is established. If the turbidity meter is not capable of that, then CP monitoring must rely on grab sampling and the guidance regarding on-line measurements can be disregarded.

Instrument set up should be as follows:

1. Install the turbidity meter according to the guidelines for the specific instrument.
    a. Make sure that the on-line instrument is calibrated as per manufacturer's recommendations.
2. Attach a constant head device or back-pressure relief valve between the sample line outlet and the turbidity meter that can split the flow in two; one flow to the turbidity meter and one flow for grab sampling.
3. Adjust the flow on the constant head device or back-pressure relief valve.
    a. Sample flow should facilitate turbulent flow conditions.
        i) For most startups, a flow of 1 L/min is the maximum possible flow.
    b. Flow to the turbidity meter must fit the requirements of the instrument.
    c. Also see Section 8.2 for discussion about sample cooler capacity.
4. The sampled water should be at or close to room temperature.
5. Make sure that the turbidity meter shows realistic results.
    a. For instance, turbidity values of 5 FNU or more should not be occurring for longer periods of time.
        i) Such a situation might indicate that the flow through the instrument is not correct, or that there are air bubbles in the sampled water.

6. Make sure that the data is recorded, i.e. either saved locally by the instrument, recorded by the DCS, or uploaded correctly to a cloud data server.
7. If the turbidity meter works as intended, it should not be touched during the startup.

Figure 8 shows an overview of how the flow settings might look during a startup, and Figure 9 shows a real setup.

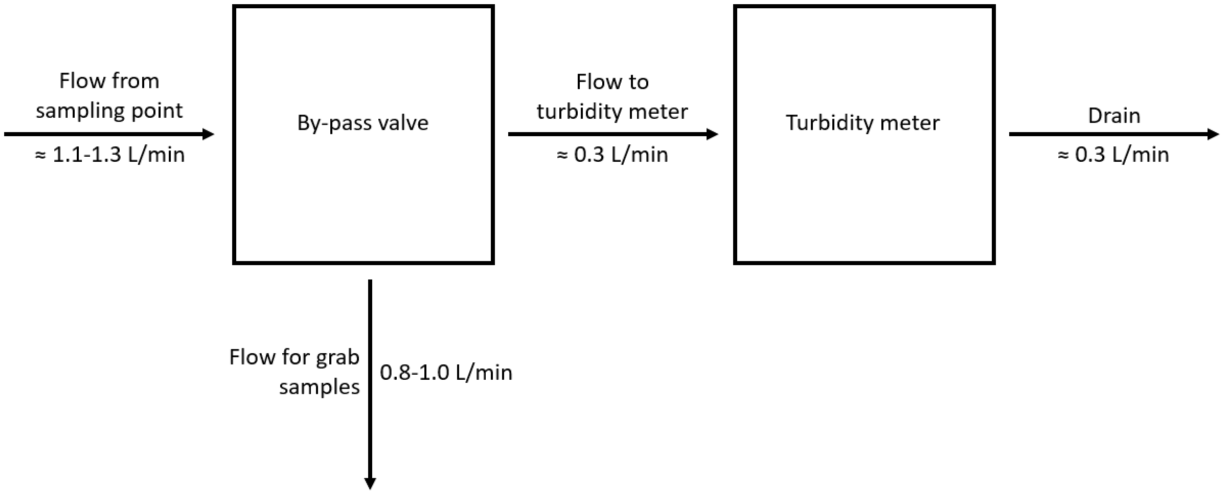

Figure 8. Schematic drawing of the sampling setup and a turbidity meter. A flow rate of around 1.1-1.3 L/min is achievable for most startups.

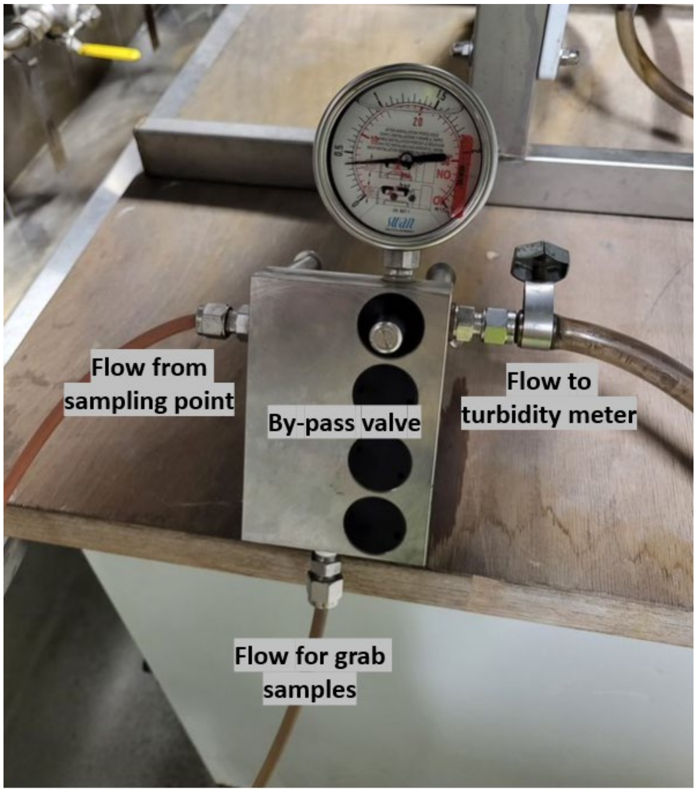

Figure 9: Picture of a real setup where the flow from the sampling point is split in two.

8.4 Sampling During Transient Load Conditions

8.4.1 Preparation

Expect to take around 15-20 grab samples (1 L) during the startup (HDPE bottles are preferred). Prepare the bottles beforehand and keep them at the sampling point.

It is very important to note the time when each sample is taken, so be prepared to do so before starting. Thereby, the concentrations of the samples can be plotted on a timeline and compared against operational changes.

8.4.2 When to Take Samples

Before and during sampling, contact should be maintained with the control room to get updates on operational changes. Generally, samples should be taken around events (milestones) that change the feedwater flow as this can increase CP transport. This often occurs at:

- Load changes
- Boiler feed pump startup
- Bringing new components such as preheaters into service or turbine run-up.

After a milestone, take 3-5 samples with about 2-3 minutes in between to follow the development of CP levels afterwards. Typically, the first events are the most interesting as the system will be flushed over time. In the case of no events take a grab sample every half hour.

Keep following these sampling guidelines until the startup is over. The startup is over when the power plant is in steady operation (defined by the operator). In some cases, CP transport may continue several hours after this point and the sampling (once per hour) should be continued until the level has decreased to near normal values. The level of CPs may be followed by the proxy method or by filtering samples and visual evaluation of filter colour along with the sampling.

8.4.3 Sampling During Online Monitoring

Sampling should be done at operational changes as described above. When an online monitoring instrument is available, sampling should also be done when the online monitoring instrument shows changes. If turbidity is being measured, a good rule is to take a sample when the turbidity changes by at least 10%. In the case of no events or no changes in turbidity, take a grab sample every half hour.

The 10%-rule overrules the rule of taking 3-5 samples after an event. Sometimes more samples may need to be taken, or otherwise if there is no change in the on-line results, then there is no reason to keep sampling. The underlying purpose is to get grab samples covering the recorded range of the online instrument to establish a good correlation between filtered iron and proxy instrument reading.

Steps for sampling:

1. When it is time to take a sample, note the start time.
    a. Also note the reading shown on the turbidity meter.
2. Fill a 1 L bottle.
3. When the bottle has been filled, note the end time.
    a. Also note the reading shown on the online instrument.
4. Repeat as many times as necessary.
    a. 15-20 grab samples are probably sufficient to cover CP transport during a startup.
    b. If the turbidity meter keeps showing changes, keep sampling.

8.4.4 Sampling Without an Online Monitoring Instrument

Sampling should be done at operational changes as described above. If a plant does not have an on-line proxy instrument installed to give an indication of changes in CP levels, then filtration of samples immediately after sampling is recommended. CP transport may then be followed by visually evaluating the filter colours. In this case, the sampling guidelines below should be followed and adjusted according to filter colours:

- After a milestone, take 3-5 samples with about 2-3 minutes in between.
- When there are no milestones, take a sample each half hour.

Steps for sampling:

1. When it is time to take a sample, note the start time.
2. Fill a 1 L bottle.
3. When the bottle has been filled, note the end time.
4. Repeat as many times as necessary.
    a. 15-20 grab samples are probably sufficient to cover CP transport during a startup.

8.4.5 Grab Sample Filtration

Filter the 1 L grab samples as soon as possible after sampling and preferably no longer than 12 hours after sampling. Afterwards, the filters can be analysed immediately to determine the amount of particulate iron, or the filters can be stored in a dry environment until the analysis is conducted.

Equipment

Standard equipment for vacuum filtration:

- Funnel/filter holder.
- Filtering flask.
- Vacuum pump/water ejector.

- Membrane filters (0.45 µm pore size) made of cellulose nitrate, e.g. from Millipore, Sartorius, or other makers.
  - The standard type used for the determination of suspended solids.
  - Membrane filters should always be handled by using a pair of tweezers; contact with fingers must be avoided.

Procedure

Filtration

1. Make sure that the volume of each grab sample is 1 L.
   a. If a grab sample has a lower volume than 1 L, note the volume as it will be used for the volume correction later.
2. Filter each 1 L grab sample through a 0.45 µm filter.
3. Analyze the filters immediately or store them for later analysis.

Storage of filters

1. After filtration, dry the filters for a couple of hours in a place protected from dust and other debris from the surroundings.
2. Put the filters in separate small containers, e.g. petri dishes or cartridges, where they are protected.
3. Store the filters in a desiccator until they are analyzed.

The filtration setup can be seen in Figure 10.

Figure 10. Filtration setup.

8.4.6 Filter Digestion and Iron Analysis

To determine the total mass of iron present on the filter, the filter requires acid digestion combined with heating then analysis via a suitable method for dissolved iron. This value is then divided by the total volume of the filtered sample to give the average total iron value for the sampling period. The various analytical methods that can be used for this purpose are summarised in TGD6-13 [1].

8.4.7 Filter Iron or Total Iron Measurement

In principle, grab samples can be analysed for total iron instead of using the filter iron method for correlating iron concentrations with proxy methods.

For both total iron and filter iron measurements, it is essential that the analytical method includes a digestion step with both acidification and heating in order to fully dissolve particulate oxides as described in TGD6-13 [1].

In this White Paper, the filter iron method is recommended instead of total iron measurement due to the following main advantages:

- Achieving a better correlation with particle based proxy methods as the filters will only collect particulate iron oxides.
- Improved method sensitivity to be able to reliably measure iron levels of < 2 ppb.
- Also provides a simple visual indication of corrosion product levels.
- If off-site analysis for iron is required, filter papers are easy to transport and there is no issue with adsorption to sample bottle surfaces.

As described previously, most iron oxides in power plant cycles are mainly present in particulate form unless there is a significant problem with active corrosion that produces dissolved iron, so a reasonable correlation between total iron and proxy measurements should be possible. If there is an issue with active corrosion at a plant, this can easily be determined by the Operator by comparing parallel measurements of filtered iron and total iron to determine if there is a significant dissolved iron fraction.

9. Assessment of Corrosion Product Transport during Startups

This section provides guidance on the treatment of data and assessment of CP levels and transport during startup. When the grab samples have been analyzed, and the data from the online measurements have been obtained, the startup data is ready to be evaluated. If turbidity has been measured, a correlation between turbidity and the concentrations of iron should firstly be established.

9.1 Establishing the Correlation Factor between Turbidity and Particulate Iron

The following procedure describes how to establish the correlation factor between online turbidity measurements and filter-Fe grab sample concentrations:

1. Use the "start time" and "end time" noted for the grab samples to calculate an average time for each sample.
2. Look up the turbidity values that have been measured from "start time" to "end time" and calculate an average turbidity value for this time period.
    a. If the minimum and maximum value of turbidity for this time period deviates more than 0.5 FNU, this data point should not be used to establish the correlation factor.
        i. Most turbidity instrument records the data once a minute meaning that the average turbidity value will be inaccurate during large turbidity fluctuations.
3. Plot the turbidity on the x-axis and iron concentration on the y-axis.
4. Perform linear regression and remove outliers.
5. Establish the correlation factor between iron concentration and turbidity.

If a strong correlation is found, it means that the online instrument can be used to give a semi-quantitative estimate of CP transport. However, it can never completely replace grab sampling and laboratory analysis. It is important to update the correlation factor when possible with more grab sampling and more data points for the linear regression.

9.2 Constructing the Startup Plot

When the correlation factor has been established, a startup plot can be constructed. In this plot, the turbidity, iron concentration and operational parameters (e.g. feedwater flow and fuel load) should be plotted. This will give an overall picture of the startup and particular events when CP transport increases.

1. The x-axis should be a time scale for the entire duration of the startup.
2. Plot turbidity on the y-axis.
3. Plot filter-Fe concentration on the second y-axis.
    a. The scale of the second y-axis should be scaled to the first y-axis by the correlation factor between turbidity and filter-Fe to make the data points for filter-Fe fit the turbidity curve.
4. Plot the operational parameters on the second y-axis.
5. Highlight milestones (first fire, start of boiler feedwater pump, synchronization etc.) in the plot to highlight which events lead to increased CP transport.

An example of a startup plot from a combined cycle/HRSG plant starting up after a summer shutdown with dry air preservation of the boiler is displayed in Figure 11. The turbidity and filter-Fe data is the same data that was used for Figure 4 where a correlation factor of 35.9 ppb/FNU was found.

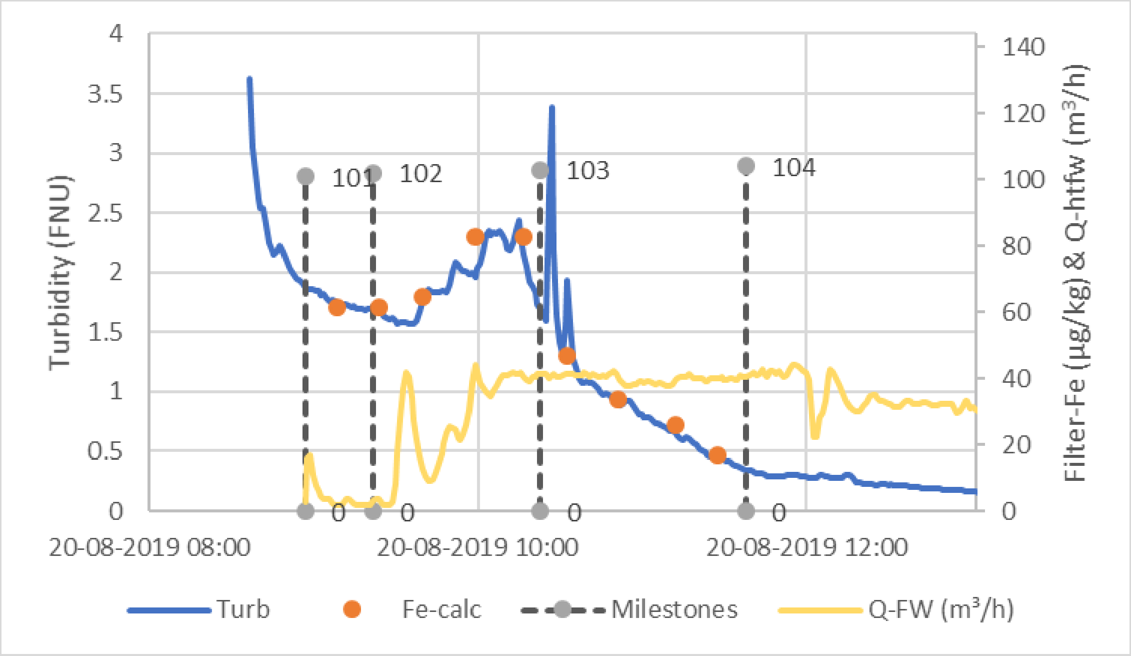

Figure 11. Turbidity and filter-Fe measured during startup of a combined cycle/HRSG plant. The milestones marked are: 101: GT fire, 102: heating of deaerator tank, 103: addition of makeup water, 104: steam turbine synchronization.

9.3 Calculating the Total Mass of Corrosion Products being Transported

If a good correlation between turbidity and filter-Fe is found, the area under the turbidity curve gives an estimate of the total amount of CPs being transported during the measurements. Thereby, the total amount of corrosion product transported can be roughly determined by calculating the area under the turbidity curve. This is calculated by the following equation:

$$m_{CP} = T \cdot Q_{FW} \cdot k \cdot \Delta t$$

- m_{CP} – total mass of corrosion products (mg)
- T – turbidity value (FNU)
- Q_{FW} – feedwater flow (kg/min)
- k – correlation factor (mg/kg/FNU)
- Δt – time interval (min)

If turbidity is measured each minute, the time interval, Δt, is 1 minute. The turbidity value and the feedwater flow for this particular time interval and the correlation factor are multiplied. This means that there will be an m_{CP} for every minute of the startup. All these values are then summed which gives the total amount of corrosion products that have been transported during the startup.

For Figure 11, 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.

9.4 Construction of the IAPWS Decay Map with Data from a Startup

To evaluate if the CP transport is acceptable or unacceptable, the startup plot can be superimposed on the IAPWS Decay Map. For this purpose, the startup point must be set to a certain event as described in Section 8.1. Practically, superimposing the startup plot onto the IAPWS Decay Map is done by the following procedure:

1. Choose an event for a startup time.
2. Adjust the x-axis of the startup plot so x = 0 is exactly at the startup time.
3. Copy the startup plot onto the IAPWS Decay Map.
    a. Make sure the startup plot is in the front.
4. Remove axes titles of the startup plot.
5. Adjust the size of the startup plot, so the scales of the axes match the IAPWS Decay Plot.
    a. This is most accurately done by using the grid lines.
6. Make grid lines, x- and y-axis, and the background transparent for the startup plot so only the turbidity curve and filter-Fe data points are shown.

This has been done with the startup plot shown in Figure 11, where GT Fire is set as the startup time. The result is shown in Figure 12.

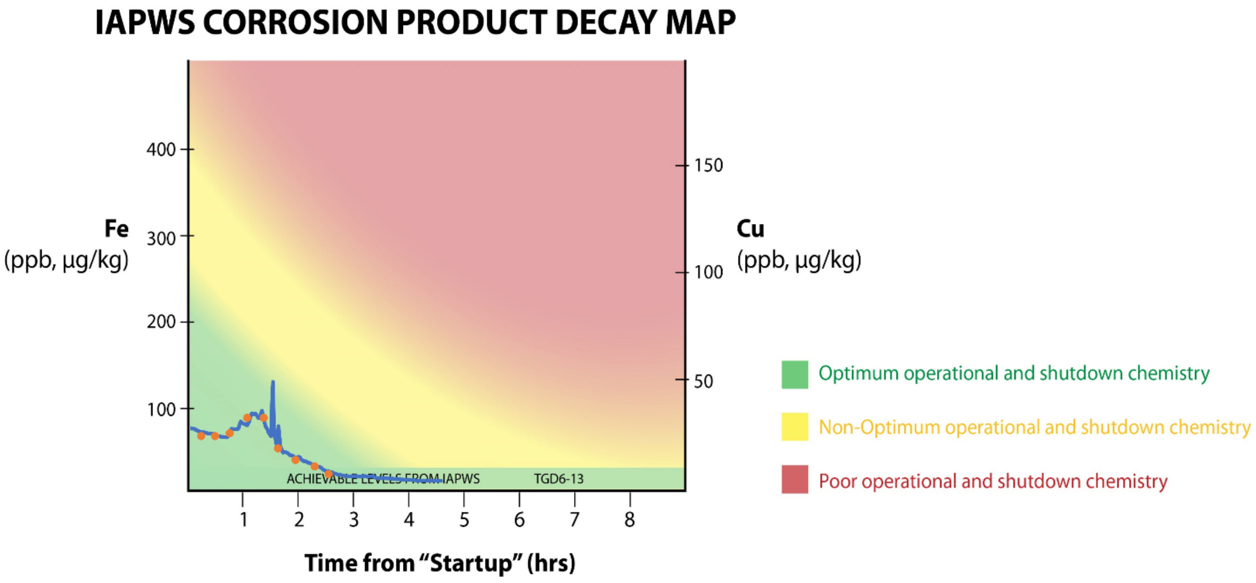

Figure 12. IAPWS Decay Map with the startup plot from Figure 11 superimposed. The CP transport remains in the green area throughout the startup meaning that the operational and shutdown chemistry is optimal.

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

10.1 Operational and Shutdown Influencing Factors for Corrosion Product Decay

Section 7 introduced the IAPWS Decay Map (Figure 7) and Figure 12 showed a Corrosion Product decay curve from a unit with good operational chemistry and good shutdown practices superimposed on the Decay Map which resulted with the decay curve being essentially in the green area. Once an operator or chemist has conducted the sampling and analysis of corrosion products as delineated in Section 8 and has produced a decay profile such as the two examples shown in Figure 12 and Appendix 2, then there is need to determine if this profile represents the lowest achievable level of transported corrosion products, or if improvements can be made to the operational chemistry and/or the shutdown protection provided. For the examples there is a need to conduct such an analysis so that the decay curves can be brought into or approach the green area without any high iron spikes.

This section of the White Paper outlines 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).

10.1.1 Supercritical Units

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

- Optimum OT chemistry for supercritical and ultra-supercritical plant as described in the IAPWS Volatile TGD [2].
- One injection point for oxygen at the condensate pump discharge (CPD).
- During operation – vents closed on LP and HP heaters and on the Deaerator (DA).
- Plant has good air in-leakage (AIL) control and an AIL Plant team [19].
- Pipework downstream of level control valves on feedwater heater drains and emergency drains checked for FAC as well as locations on heater shells where cascading drainage enters [20].
- 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 [2].
- During longer shutdowns (more than a week), the surfaces are protected with N_2 blanketing, dehumidified air (DHA), by pH elevation, or by the use of FFS during operation [7].

Indications of non-optimum chemistry on these units (corrosion product profiles in the Yellow and/or Red areas)

- OT chemistry for supercritical and ultra-supercritical plants does not follow the IAPWS Volatile TGD [2], with vents on heaters and/or DA not fully closed or leaking.
- Poor AIL control and no AIL plant team [19].
- Continued use of AVT(O) with insufficient oxygen to completely passivate all the feedwater surfaces [2] to result in ruggedly red water-touched surfaces.
- Use of AVT(R) (IAPWS is aware that some supercritical units worldwide operate with AVT(R). This is due to a complete misunderstanding about oxide growth and exfoliation in steam which is thought to be influenced by oxygen levels whereas there is no influence [21]).
- No short-term or longterm shutdown/layup protection using N_2 blanketing, DHA, or by the use of FFS during operation [7].
- Leaving water circuits (feedwater and boiler water) 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 makeup 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.

10.1.2 Drum Units (with all-ferrous feedwater systems)

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

- Optimum AVT(O) or OT chemistry as described in the IAPWS Volatile TGD [2].

- If operating on OT during operation – vents closed on LP and HP heaters and on the DA. One injection point for oxygen at CPD.
- Plant has good air in-leakage (AIL) control and an AIL Plant team [19].
- Pipework downstream of level 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 [20].
- 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 N_2 blanketing, DHA, by pH elevation, or by the use of FFS during operation [7].
- Water circuits are periodically circulated during longer-term shutdowns to prevent localised corrosion cells becoming established.

Indications of non-optimum chemistry on these units (corrosion product profiles in the Yellow and/or Red areas)

- Continued use of AVT(R) chemistry with addition of a reducing agent (see customization Section 11).
- AVT(O) or OT chemistry does not follow the IAPWS Volatile TGD [2], with vents on heaters and/or DA not fully closed if using OT.
- Poor AIL control and no AIL plant team [19].
- 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 [2].
- Conversion to AVT(R) during shutdown.
- No short-term or longterm shutdown/layup protection using N_2 blanketing, DHA, by pH elevation, or by the use of FFS during operation [7].
- 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 makeup 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.

10.1.3 Drum Units (with mixed-metallurgy (copper) feedwater systems)

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

- Plant operates with optimum feedwater chemistry control for mixed-metallurgy units [2, 20].
- Feedwater chemistry is AVT(R) as described in the IAPWS Volatile TGD [2].
- Plant has good air in-leakage (AIL) control and an AIL Plant team [19].
- Monitors oxidation-reduction potential (ORP) at deaerator inlet and operates under reducing conditions.
- Pipework 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 [20].
- Minimizes any change of chemistry during shutdowns especially with no increases in condensate/feedwater oxygen and pH.
- Feedwater during shutdowns remains AVT(R).
- During longer shutdowns (more than a week), the feedwater and boiler surfaces are protected with N_2 blanketing, DHA, by pH elevation, or by the use of FFS during operation [7].
- Water circuits are periodically circulated during longer-term shutdowns to prevent localised corrosion cells becoming established.

Indications of non-optimum chemistry on these units (corrosion product profiles in the Yellow and/or Red areas)

- Plant operates with non-optimum feedwater chemistry control for mixed-metallurgy units [22] and outside the regime described in the IAPWS Volatile TGD [2].
- Plant has poor air in-leakage (AIL) control and no AIL Plant team [19].
- No monitoring of ORP at deaerator inlet and operates under oxidizing conditions.
- No inspections or monitoring for FAC in condensate and feedwater systems and with iron and copper levels exceeding the IAPWS guidance [20].
- No control of chemistry during shutdowns especially allowing oxidizing conditions (increase of feedwater/condensate oxygen and no reducing agent). Feedwater changes to AVT(O).
- During longer shutdowns (more than a week), the feedwater and boiler surfaces are not with N_2 blanketing, DHA or by the use of FFS during operation [7]
- Water circuits are not periodically circulated during longer-term shutdowns to prevent localised corrosion cells becoming established.

10.1.4 Combined Cycle/HRSG Plants

It is noted that for the other plants (Sections 11.1.1 – 11.1.3) the IAPWS decay profiles relate to feedwater corrosion products at the economizer inlet. For combined cycle plants, the IAPWS Guidance [1, 2] also provides achievable levels in the drums. Thus, optimum chemistry control on the Decay Map is applicable to the HP/IP economizer inlet (boiler feed pump). Currently there is not a decay map for the drum monitoring locations on HRSGs.

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

- Use of AVT(O) chemistry (or OT) which follows the IAPWS Volatile TGD [2].
- No reducing agent is added to the plant.
- The pH is optimized through a monitoring campaign [1, 2, 23].
- Use of phosphate treatment (PT) or caustic treatment (CT) for the drums and evaporators which follows the IAPWS TGD4-11 [3].
- Single- and two-phase FAC assessments have been made for typical areas of FAC in HRSGs [20, 23].
- Low levels of HP Evaporator Deposits according to IAPWS TGD (< 25 mg/cm^2 or within the green/yellow band on IAPWS TGD7-16 HRSG HP Evaporator Deposit Map) [23, 24].

Indications of non-optimum chemistry on these units (corrosion product profiles in the Yellow and/or Red areas):

- Use of AVT(R) chemistry [2, 23].
- Incorrect usage of PT or CT [3, 23]. In the former, this might involve using other than tri-sodium phosphate (operating with a Na:PO4 molar ratio < 3 [5]) or an unknown proprietary phosphate blend.
- High levels of HP Evaporator Deposits according to IAPWS TGD (> 25 mg/cm^2 or within the red band on IAPWS HRSG HP Evaporator Deposit [23, 24]).
- Poor AIL control and no AIL plant team [19].
- No shutdown protection (N_2, DHA, FFS) with multiple potential 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) plants with unpredictable generation dispatch with unexpected extended standing periods waiting for system control (initially X days/hours shutdown moves to multiples of X).

11. Customization and Understanding of Corrosion Product and Decay Profiles

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 Sections 7 and 10 has been developed for 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 different to those in Sections 7 and 10. 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 and 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.

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 other plants and equipment as there cannot be one set which can be applied to every plant worldwide.

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

Although it is very clear in the IAPWS TGD [2] that units with all-ferrous feedwater systems should operate only with oxidizing feedwater treatments, there are still over 35% of these units worldwide continuing to operate with AVT(R) [23]. 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 12 and Section 10. It is also well understood that the possibility of single-phase FAC increases drastically when these units operate under reducing conditions [20]. The factors contributing to this are very similar to the factors delineated in Section 10.1.2 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 [2].
- Poor AIL control and no AIL plant team [19].
- Use of reducing agent during shutdown when operational chemistry is AVT(O).
- Conversion to AVT(O) during shutdown.
- No short-term or longterm shutdown/layup protection using N_2 blanketing, DHA, by pH elevation, or by the use of FFS during operation [7].

11.2 Conventional Drum Units with Copper Feedwater Systems

This sub-section is generally applicable to older units with copper alloys in the feedwater system. 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 [22]. 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 [22]. 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 TGD for Volatile Treatments [2], 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 methods (Section 5) 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 as well as the economizer inlet.

A typical copper oxide corrosion product decay curve was shown in Figure 1 based on actual data [4] 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 cases in Section 10.

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

- Optimum AVT(R) chemistry is as described in the IAPWS Volatile TGD [2] and [22].
- 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 [19].
- 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 [7]. 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.

<u>Indications of non-optimum chemistry on these units (corrosion product profiles in the Red area);</u>

- 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 an FFS is not used during operation.

11.3 Units with an Air-cooled Condenser (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 ACCs at the lower regimes of pH provided in the IAPWS Volatile TGD [2] may result in serious corrosion and FAC in the ACC tubes, most predominantly at the entries to the cooling tubes [25]. Whether this is occurring can easily be determined by monitoring the total iron at the condensate pump discharge (CPD) [20, 25]. 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) [25, 26] 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 7. 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 [7, 20, 25]. 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 [25, 26], 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 methods (Section 5) 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 7 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 [25, 26].

11.4 Units using Film Forming Substances (FFS)

The application of an FFS is one of the recently introduced chemistries which are claimed to reduce corrosion product transport and to provide shutdown protection. IAPWS has introduced a TGD [7] to address all aspects of applying FFS to generating plant. But todate there has been no comprehensive method of confirming the corrosion product levels before and after application of an FFS. The proxy monitoring method described in previous sections of this IAPWS White Paper together with superimposing the decay curve on the Decay Map provide the necessary information to validate or otherwise any benefits associated with the application. The use of an FFS for shutdown protection can also be appraised by applying the proxy analysis during startup or return to service, and overlaying of the decay curve on the Decay Map. In both cases improvements in total iron transport will be noted by lower decay curves (within the green area of Figure 7).

The presence of FFS in the sample may have an impact on the optical surface of the online instruments (turbidity, particle counter/monitor) used as proxy methods.

11.5 Variability of Shutdown Durations and Speed of Return to Service

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 shutdown 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 [2, 3], 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 7. 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. 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.

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 10.1, 11.1 and 11.2.
- Improving appropriate shutdown/layup chemistries as described previously (Section 10). 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 Decay 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 [27].
- 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 [20] 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 [2, 26]. The amended IAPWS TGD on Instrumentation [25] 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.

11.6 Corrosion Product Monitoring in Boiler Water Samples

The monitoring of corrosion product levels in boiler water / HRSG drum water samples is a key requirement for assessing the effectiveness of a water-steam cycle chemistry program.

The methodology recommended in this White Paper for corrosion product monitoring can also be applied to these samples and used to evaluate operational and shutdown chemical conditions and the effectiveness of optimization measures to reduce corrosion product transport into boilers. A further potential application is supporting the monitoring of FAC management in lower pressure boiler / HRSG evaporator circuits.

It should be recognized that the IAPWS Decay Map has been developed specifically for feedwater monitoring at the economizer inlet and there is no equivalent map for boiler water. However, by monitoring and comparing corrosion transport profiles using the IAPWS methodology, Operators can use this approach to evaluate the effect of plant improvements towards optimizing chemical control.

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Appendix 1: IAPWS Decay Map

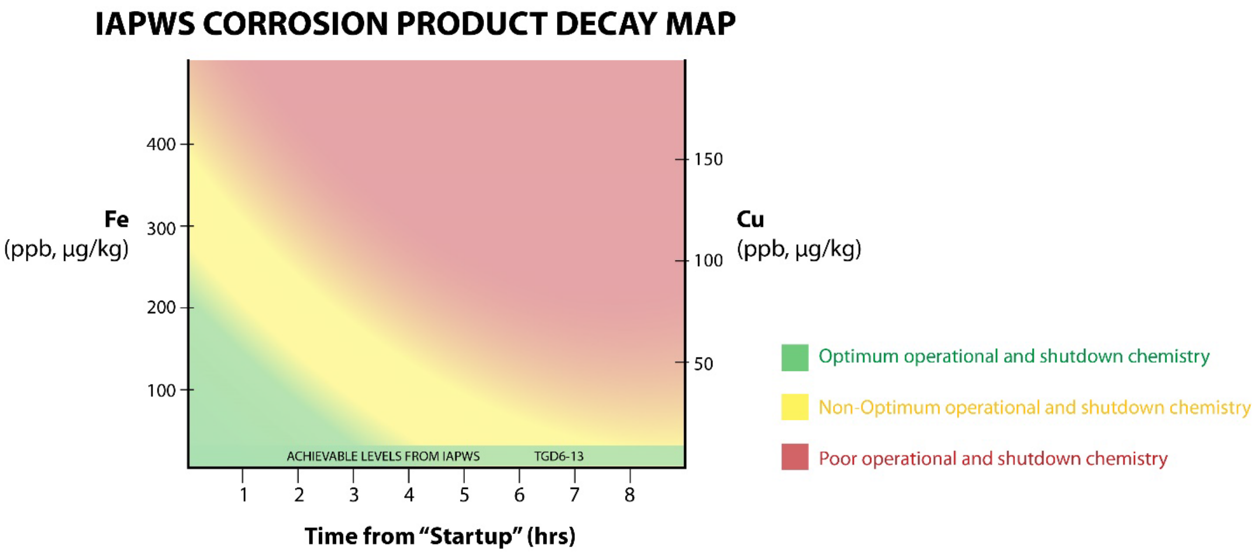


Figure A-1. The IAPWS Corrosion Product Decay Map.

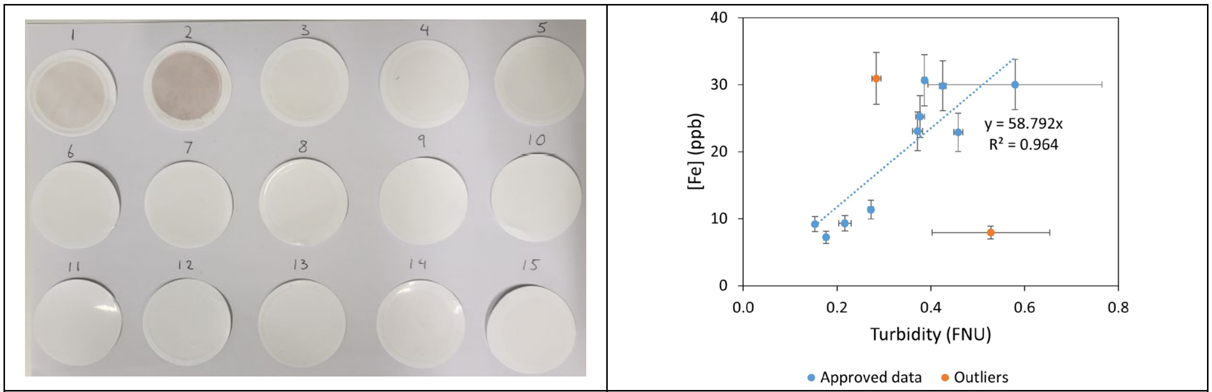
Appendix 2. Examples of Decay Map

In this section, examples are presented of the key outputs from the application of the IAPWS methodology for monitoring and assessing CP transport at startup and under transient operating conditions [14]. This brings together and highlights the complete approach from filter samples, correlating corrosion product levels with proxy methods, plant decay profiles, and finally, superimposing on the IAPWS Decay Map for benchmarking. The main features of the decay profiles are the deviations above the green area of the map for operators to use to prompt investigation of possible deficiencies in operational and shutdown chemistry.

A2.1 Startup Decay Profiles

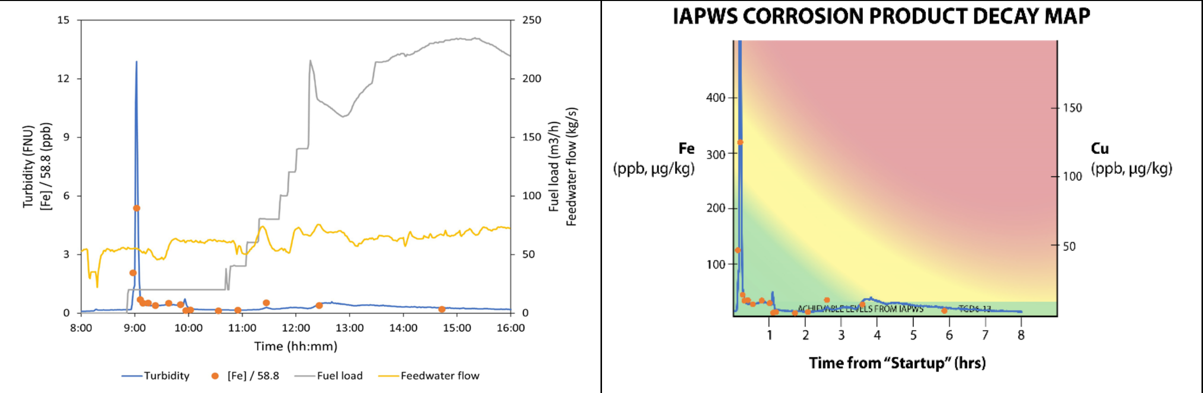
A2.1.1 Plant A – Startup After Seasonal Shutdown

Plant A is a biomass-fired power plant with all-ferrous feedwater system metallurgy and AVT(O) feedwater chemistry. The CP monitoring exercise was completed during the unit startup after the summer shutdown during which the water-steam cycle was preserved dry. The results are shown in Figure 13. The economizer inlet was the sample point.



Filter samples

Correlating iron concentration and turbidity



Plant startup data

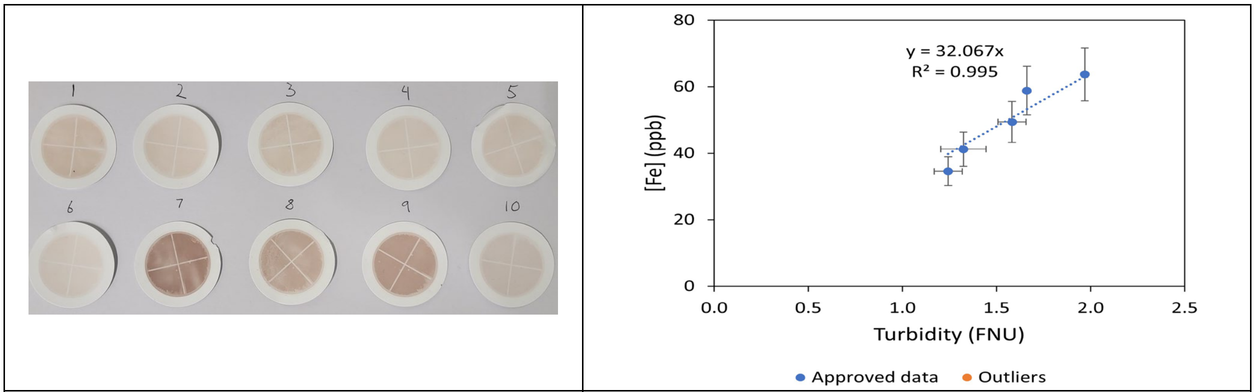
Superimposing on the IAPWS Decay Map

Figure 13. Plant startup after seasonal shutdown (all-ferrous feedwater system, AVT(O) feedwater chemistry, dry preservation). First load increase is set as the startup time for the IAPWS Decay Map.

After a large spike in turbidity just after the first load increase, the turbidity rapidly declines to low levels. Superimposition on the IAPWS Decay Map shows that CP transport drops rapidly into the green area such that the operational and shutdown chemistry at the plant has been relatively good overall. The short-term spike into the red area during the early startup phase suggests that there has been a slight buildup of corrosion products that might have been formed during the shutdown period if there were localized areas that were not completely dry.

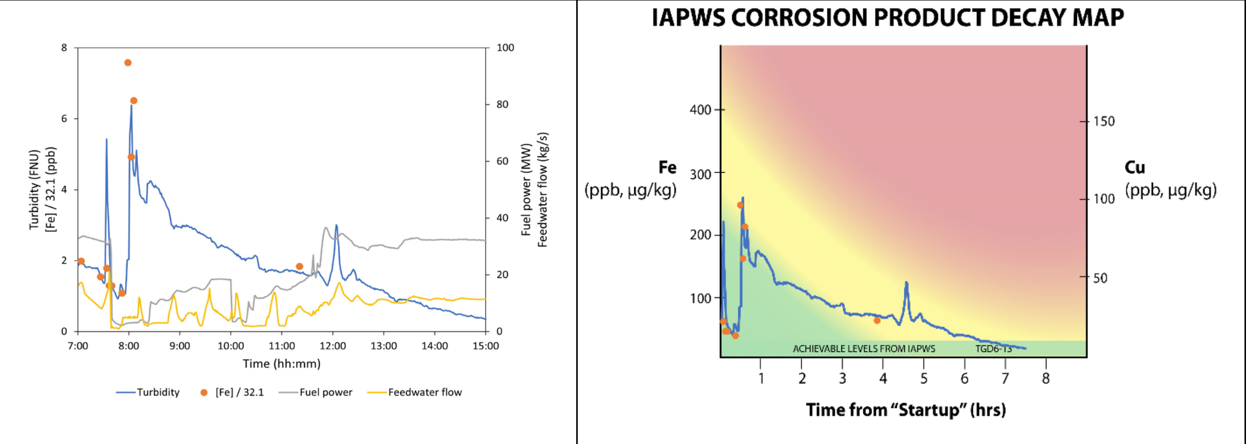
A2.1.2 Plant B – Startup After Seasonal Shutdown – No Preservation

Plant B is also a biomass boiler with an all-ferrous feedwater system, AVT(O) feedwater chemistry and summer plant shutdown. In this case, there was no preservation of the water-steam cycle during the shutdown period. The results of monitoring before the subsequent plant startup are shown in Figure 14. In fact, this measurement campaign captured a boiler shutdown and boiler startup at around 7:30 and 8:00, respectively, as the plant faced operational difficulties during the startup procedure that required a restart of the boiler. The feedwater sample point was used.



Filter samples

Correlating iron concentration and turbidity



Plant startup data

Superimposition on the IAPWS Decay Map

Figure 14. **Plant startup after seasonal shutdown (all-ferrous feedwater system, AVT(O) feedwater chemistry, no preservation). Boiler shutdown is set as the startup time for the IAPWS Decay Map.**

Whilst iron levels remain mainly in the green and yellow areas of the IAPWS Decay Map, the plant operates for almost 8 hours in the yellow area where the operational and shutdown chemistry is considered non-optimal. The large area under the turbidity line suggests reasonable cumulative iron transport into the boiler from this event. The elevation compared to Plant A is clear. This situation could obviously be improved by preserving the water-steam cycle during the shutdown period.

A2.1.3 Plant C – Copper Alloys in the Feedwater System

Plant C is a coal-fired unit with copper alloys in the condensate and feedwater system. The feedwater chemistry is AVT(O) with a film forming substance (FFS) (recognising that AVT(R) feedwater chemistry would normally be recommended for a mixed metallurgy system). Corrosion product monitoring was completed during unit startup after a 4-day shutdown with no other method of preservation. The results are shown in Figure 15. The economizer inlet was the sample point.

For power plants with mixed metallurgy feedwater systems, turbidity depends on both the iron and copper concentration. This is expressed by the following equation:

$$T = a \cdot [Fe] + b \cdot [Cu]$$

Countless combinations of a and b can be found for a sample where turbidity and the concentration of iron and copper is known. However, the goal is to establish one correlation factor relating the iron concentration to the turbidity and one correlation factor relating the copper concentration to the turbidity. To do so, the copper concentration must be plotted against the iron concentration to test for a linear correlation. If a strong correlation is found, the copper concentration can be expressed as a function of the iron concentration and vice versa. This can be seen in the equations below where k_1 is the correlation factor found when plotting the copper concentration against the iron concentration.

$$[Cu] = k_1 \cdot [Fe]$$

$$[Fe] = \frac{[Cu]}{k_1}$$

Turbidity can then be expressed as:

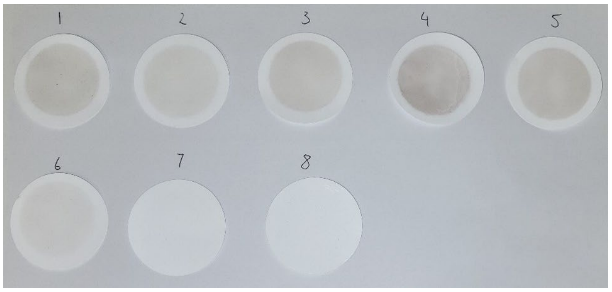
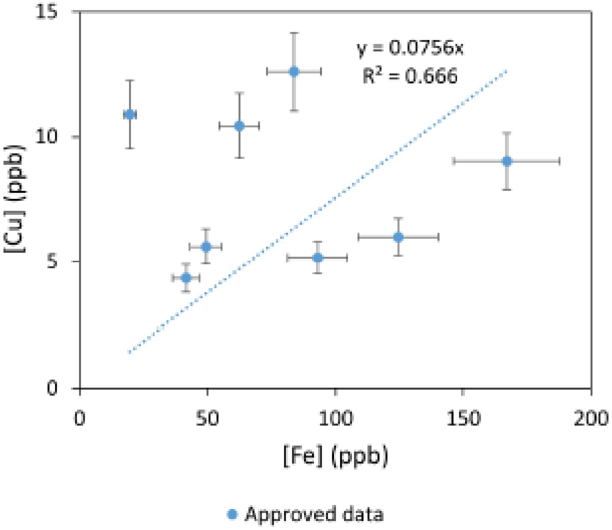
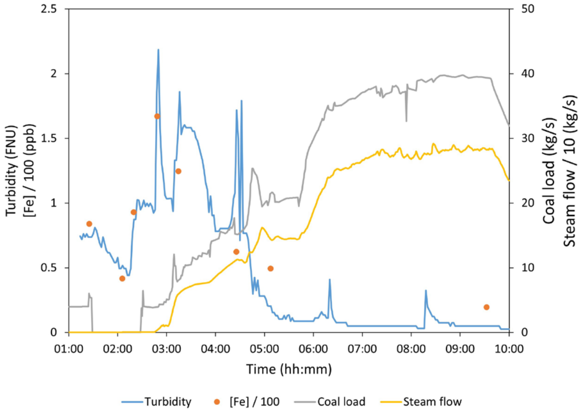
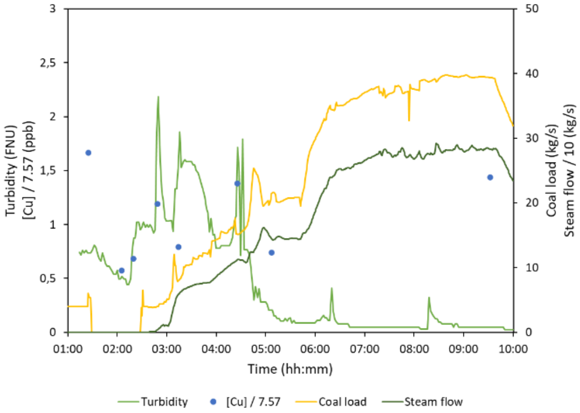
$$T = a \cdot [Fe] + b \cdot k_1 \cdot [Fe] = (a + b \cdot k_1) \cdot [Fe]$$

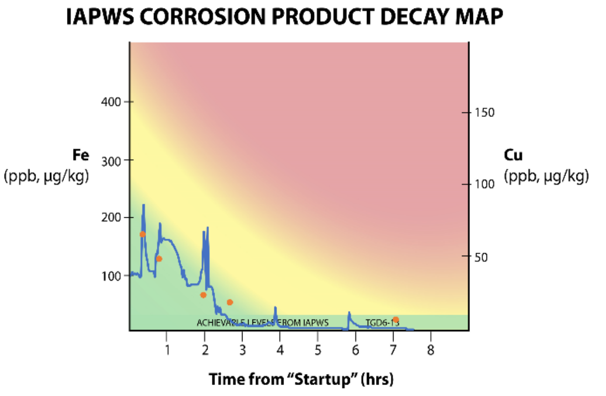
or

$$T = a \cdot \frac{[Cu]}{k_1} + b \cdot [Cu] = \left(\frac{a}{k_1} + b\right) \cdot [Cu]$$

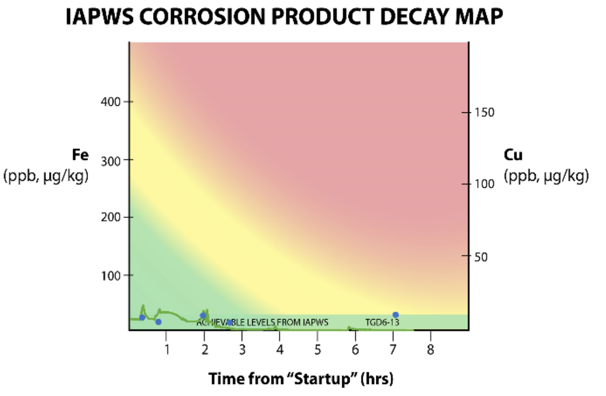
By multivariable regression with the iron and copper concentration as the two independent variables, a and b can be found. Thus, the correlation factor between the iron concentration and turbidity, $(a + b \cdot k_1)$, and the correlation factor between the copper concentration and turbidity, $\left(\frac{a}{k_1} + b\right)$, can be calculated. This way, the contribution to the turbidity from copper particles is taken into account when only looking at the iron concentration and vice versa [14].

From this data, the correlation between the copper concentration and iron concentration is poor. However, the results are shown anyway to illustrate an example of a poor correlation.

	
Filter samples	Correlation between [Cu] and [Fe]
	
Plant startup data (Fe)	Plant startup data (Cu)



Superimposition on the IAPWS Decay Map (Fe)



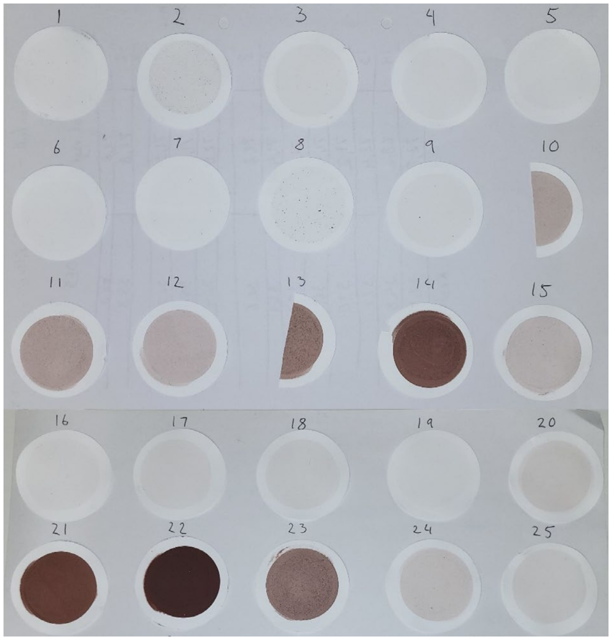
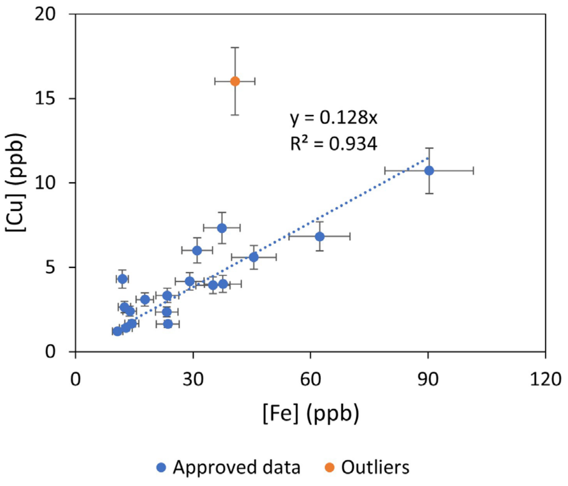
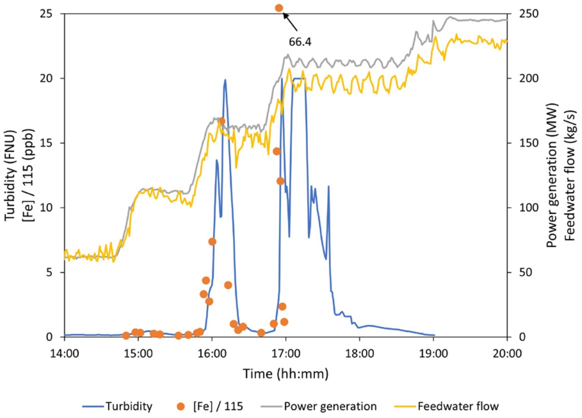
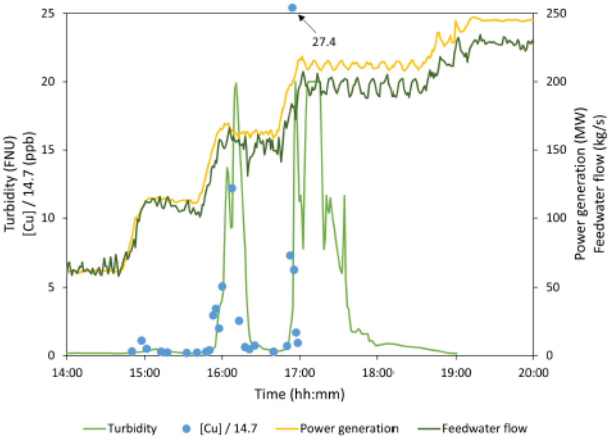
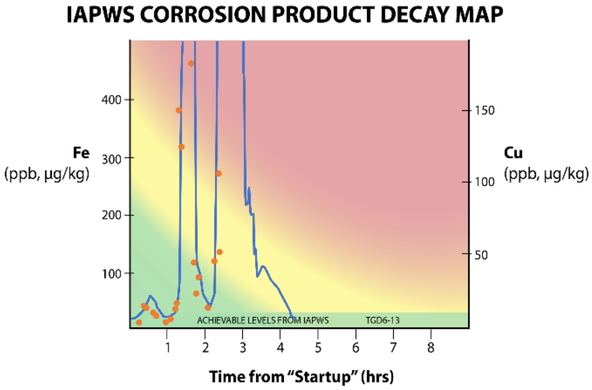
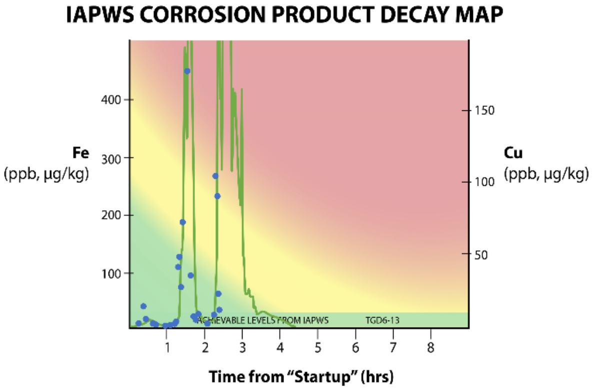
Superimposition on the IAPWS Decay Map (Cu)

Figure 15. Plant startup after 4 day shutdown (mixed-metallurgy feedwater system, AVT(O) feedwater chemistry with film forming substance). The first increase of coal load is set as the startup time for the IAPWS Decay Map.

From the IAPWS Decay Map, it can be seen that the transport of both iron and copper corrosion products is relatively low during the startup. Iron transport decreases with time after the initial unit startup reaching low levels after around 2.5 hours. This is likely to be due to the use of the film forming substance given the feedwater system metallurgy and absence of other preservation methods.

A2.2 Monitoring Transient Conditions during Continuous Operation

Plant D is a gas-fired boiler that operates continuously but with daily load cycling. The unit has a brass condenser; otherwise the feedwater system is all-ferrous and feedwater chemistry is AVT(O). The corrosion product monitoring exercise was completed after a period of 4 hours at steady load following which unit output was increased in four 60 MWe increments up to 250 MWe. The results are shown in Figure 16. The economizer inlet was the sample point.

	
Filter samples	Correlation between [Cu] and [Fe]
	
Plant startup data (Fe)	Plant startup data (Cu)
	

Superimposition on the IAPWS Decay Map (Fe)	Superimposition on the IAPWS Decay Map (Cu)

Figure 16. Daily load cycling (all-ferrous feedwater system and brass condenser, AVT(O) feedwater chemistry)

Due to the stepwise load increments, the plant data can be usefully superimposed on the IAPWS Decay Map in this case. This shows that there are significant amounts of iron and copper corrosion products being transported into the boiler from multiple events over an extended period of time. This is unlikely to have been evident if corrosion product monitoring was limited to manual grab sampling at steady state. Because of the severity of the excursions, the results should be used by the operator to improve the operational chemistry to move towards more optimized conditions.