SIAPWS Newsletter 2017-2

IAPWS TGD on Corrosion Product Sampling and Analysis

Scandinavian branch of the International Association for the Properties of Water and Steam

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Analysis of iron or copper in water-steam circuits is the means to optimise the conditioning of the system and to document that the chosen setup is effecient. Showing and discussing the iron results with the operational guys motivates them to keep up and care for the conditioning. IAPWS recommends running a few campaigns for corrosion products (CPs) per year, rather than doing routine analyses daily or weekly. **Correct sampling and analysis of CPs is critical to get results that can be interpreted in relation to the conditioning**. This is what the IAPWS TGD on corrosion product sampling and analysis is all about.

The TGD from 2015 covers design of proper sampling systems for corrosion product sampling and on-line monitoring. Furthermore, the TGD gives guidance on the following steps: Digestion, analysis, and quality control. The users have received the TGD very well, and it is now the basis for monitoring CP formation and transport in water-steam cycles at many power stations worldwide. The TGD specifies sampling conditions under high and stable load. However, for many boilers this seldom occurs, since flexible operation (cyclic operation) and even daily start-stops are the demands of the electricity marked. Many users have asked for guidance concerning flexible plants: Does it make sense to measure CPs at all, since steady-state conditions are never obtained? If you do measure, how should the results then be interpreted? A revision of the TGD trying to meet these questions is now under way – hopefully, it will be released following the next annual IAPWS meeting in September 2017 in Kyoto.

During the next couple of months, the task group responsible for the revision would like to run parallel sampling and analysis trials at several water-steam circuits. The purpose is to cover "white spots" on the "map of knowledge" related to CPs under flexible operation. The focus is on: Transport of CPs during startup and flexible load, test of on-line methods to track these non-steady states, test of semi-quantitative filtration methods for the same purpose also. In addition, the intention is to be able to guide with respect to the uncertainty associated with corrosion product sampling. The usual perception of this is that even though the analysis methods may be rather precise, the overall precision is relatively poor due to random errors introduced by the particulate nature of the CPs and contributions from the sampling system itself. It is common that 10-20 % of the results in a series of measurements are significantly higher than the level defined by the bulk of results. It is common practise to disregard the "outliers" and base the evaluation on the level defined by the remaining results. Experience gained over the last few years and the outcome of the first, preliminary TGD sampling and analysis trial now suggest that most of the high values actually are valid data representing the true distribution of particles in the samples. The basis of the discrepancy of the ”outliers” is the standard assumption that the results follow the normal distribution as most other laboratory results do. The new insight points out that the log-normal distribution may be much more appropriate for evaluating and interpreting corrosion product measurements.

Figure 1 shows a series of 100 iron analyses in condensate with the characteristic variability well known from practice. Most of

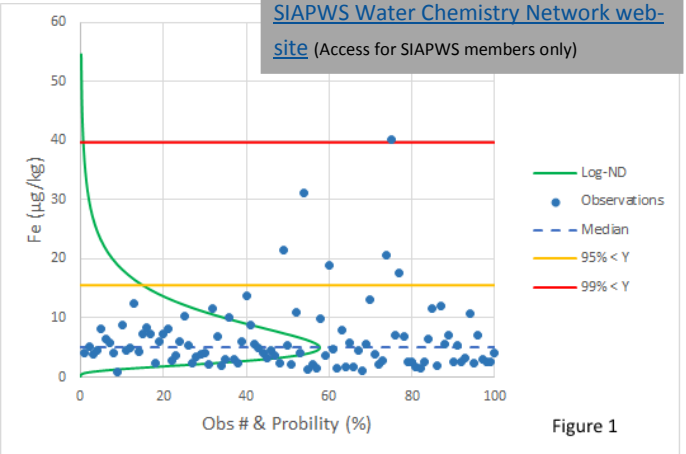

Figure 1

If you are interested in the IAPWS sampling and analysis field trials or even want to join, please contact Karsten Thomsen.

If you have questions regarding SIAPWS or the SIAPWS Water Chemistry Network, please feel free to contact the any of the SIAPWS Committee:

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Links:

Corrosion Products Sampling and Analysis TGD

SIAPWS open website (@Matarvattensektion.se)

SIAPWS Open Facebook Group

SIAPWS Member Facebook Group

SIAPWS Water Chemistry Network website (Access for SIAPWS members only)

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the result are on a low level, but quite a few are much higher. In this case, the data are not real, but are simulated from the log normal distribution depicted on the y-axis. The two control limits in the graph show the 95 % and 99 % percentage levels, respectively, *i. e.* the levels that 95 and 99 % of the results are less than. The 95 % percentage (95 % < Y) seems well suited as an operational control limits. Stable conditions with respect to formation and transport of CPS may be assumed when in average only one result in 20 is above this limit. If the relative number of high results increases over a period, the conditions are no longer stable, and the formation or transport rate has changed.

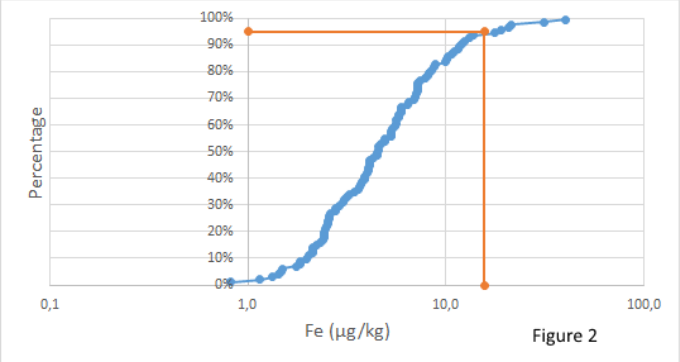

Figure 2

How do you check, if a series of CP measurements follows the log normal distribution? This is simple: Sort the data in increasing order and calculate the percentage as the rank (number in ordered series) divided by (total number + ½), then plot the percentage versus the results using a logaritmic X-axis. If the data is distributed according to the log-normal distribution, a nicely S-shaped curve appears as shown in Figure 2 where the data from Figure 1 is presented this way. Furthermore, the orange lines show how the 95 % percentage is read from a set of experimental data. This curve may easily be compared to the theoretical curve calculated from the mean and standard deviation of the log-transformed values. Figure 3 shows an example for iron measured in feed water by routine analyses over two periods. When analysed as described above, two distributions following the log-normal distribution appears. The 95 % percentages are alike around 15 ug/kg. However, the steepness of the curves are quite different indicating that there has been a change towards higher CP levels and thus higher median values over the years. Over the same period, the operational mode changed from all year flexible load operation towards fewer operational periods with lay-up times from a few days to a few weeks in between. Thus, there seems to be a correlation between the change in operational mode and the change in the distribution of CP results.

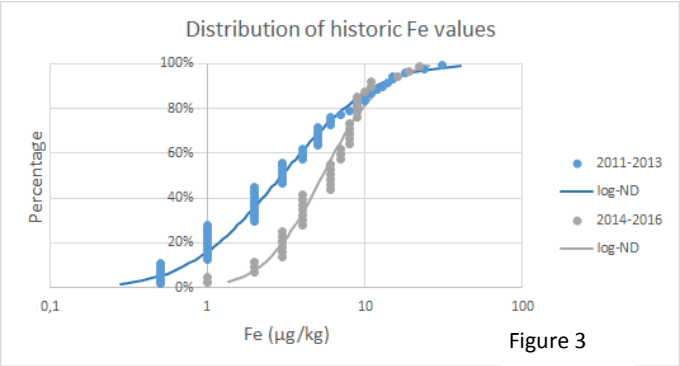

Figure 3

This data treatment may also be used to dig out the capability of your analysis method. Figure 4 shows the results of a series of feed water samples taken over half an hour. The distribution curve clearly has two parts: The part at the higher values nicely adheres to a log-normal distribution curve, whereas the lower values all lie within a rather narrow interval. The breakaway from the curve exhibits the limitations of the analysis method. It is simply not able to resolve the true content of the samples, but smears it randomly out below the quantification limit at 1 ug/kg. Note that in real life, most of the higher values containing information on the distribution of the results would be discarded as outliers, and the mean level be estimated on the smeared out values below or just above the quantification limit. This is hardly the best way to extract knowledge from your data set?

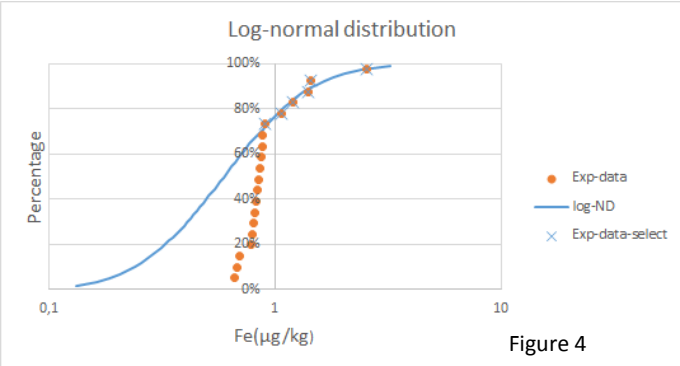

Figure 4