Real-Time Corrosion Product Transport Monitoring Using Online Particle Monitors

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ABSTRACT

This paper introduces the particle monitor as an effective means for continuously sensing and tracking the corrosion product transport. Transient metal oxides, in their insoluble particulate form, can be detected with the particle monitor. When such corrosion product transport monitoring methods are utilized, real-time particulate measurement can be implemented as an additional core parameter for operating and controlling the power plant cycle.

INTRODUCTION AND BACKGROUND

Corrosion continues to be a major concern of power plant chemists throughout the world. Steam cycle corrosion not only results in metal loss within the system, but also results in the formation of corrosion products. If not controlled, these products (soluble metals and insoluble metal oxides) can be transported within the cycle and lead to deposition. Such deposition can affect the efficiency of the plant, create a need for chemical cleanings, and, in the worst case scenario, result in catastrophic equipment failures. Treatment programs are established to minimize corrosion, but corrosion still happens.

The question becomes, "When and where is corrosion taking place, and how much of it is there?" Various equipment inspections during plant outages can reveal the extent of past corrosion activity, but estimating the degree of any active corrosion in the steam cycle at a given time during plant operation is a great challenge.

Traditional control parameters for boiler treatment programs include pH, dissolved oxygen, ORP, and conductivity. Out of range values can be indicative of a potentially more corrosive system environment, and when any of the results are found to be out of range, corrective measures must be taken in order to bring the measured value back into its respective control range. By maintaining the proper values as dictated by the treatment program, the corrosion will hopefully be minimized. But these parameter trends (individually or collectively) only indicate the potential for corrosion, and do not quantify the direct results of corrosion.

Corrosion product transport monitoring is of great concern and interest to the plant chemist. Corrosion product transport monitoring in power plants has traditionally been handled in a couple of different ways:

- Grab sample analyses
  sample is analyzed for soluble and insoluble metals; results only represent levels from a "snapshot" in time
- Composite filter pad
  a continuous sample is run through a pad for a set period of time (hours or days); the pad is removed and digested for metals analysis; results represent a composite measurement that offers an average particle loading for the duration of its installation; resin-impregnated filters can also be used which will indicate average soluble iron concentration as well.

However, with each of these approaches, there is a significant lag time between when the sample or filter pad is taken from the system and when the results are reported. Therefore, neither approach can be considered a viable control parameter.

It is commonly accepted that approximately 90 % of corrosion products in the power plant cycle consist of insoluble particulates, and only about 10 % consist of soluble metals. Therefore, by measuring the particle loading, the plant chemists can associate a quantitative value with the level of a majority of the corrosion products that are being transported through the system.

A simple, reliable system that can give online, continuous information is most always preferable to an approach that only delivers snapshots or provides long-term averages. So an online analyzer that is capable of detecting low levels of particulates would provide a solution for continuously monitoring corrosion product transport. This would allow control actions to be taken based on current corrosion product levels, followed by immediate measurements of the effect of the adjustments on corrosion product levels.

EQUIPMENT

Online particle analyzers provide instantaneous indication of particulate loading and allow continuous data collection and trending. Such equipment complements existing online ionic analyzers by adding another means of contaminant detection.

The most common method for indicating the levels of suspended solids in water is nephelometric turbidity measurement (Figure 1). However, turbidimeters utilize a light scattering means of analysis and do not have the sensitivity capabilities for accurately detecting the ppb levels of transient metal oxides that are found in the steam cycle. Also, the low-reflection properties that are typical of metal oxides make it difficult for turbidimeters to detect such particulates.

Figure 2 shows the basic principle of the particle detection technology. The particle counter is an online instrument that uses a laser light source to detect insoluble particulates in a flowing water sample and determine their respective sizes. As the sample stream flows through the laser path, particles cast shadows on a light detector. The instrument is calibrated to be able to assign each particle to a size range based on the size of each shadow (for example, 2–5 µm, 5–10 µm, 10–15 µm, etc.). The data is then expressed in particles per mL, for each size range. The particle counter has the sensitivity to detect one 2 µm diameter particle per mL, which equates to < 10 $ng \cdot L^{-1}$ (ppt) on a volumetric basis.

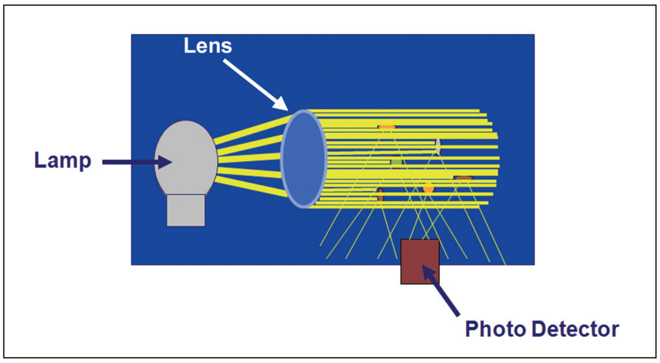

Figure 1:
Turbidity monitor – basic scheme.

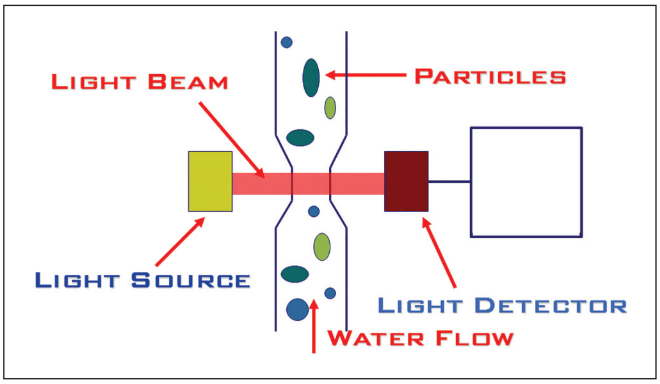

Figure 2:
Particle detection technology.

The particle monitor also utilizes a "light blockage" approach, and provides a relative indication of very low concentrations of particulate impurities. However, unlike the particle counter, it is not possible to derive absolute information on particle size or concentration. Instead, the results are expressed as a particle index. Essentially, water flows through a transparent plastic tube and is illuminated by a narrow beam of infrared radiation. A sensitive detector monitors the transmitted radiation and the output from the detector is converted to a voltage, which in turn is interpreted into the particle index. It also has the sensitivity to detect one 2 µm-diameter particle per milliliter, and can be over 100 times more sensitive than conventional nephelometric turbidimeters.

The particle monitor will trend directly with the total counts provided by a particle counter. Often times the plain and simple approach of the particle monitor is chosen over the more complex particle counter, especially when particle size and count data are not essential.

Figure 3 shows a comparison of a particle counter, particle monitor, and turbidity monitor using AC fine test dust.[1] From Figure 3 it is clear that particle monitoring is markedly superior to the turbidity monitoring.

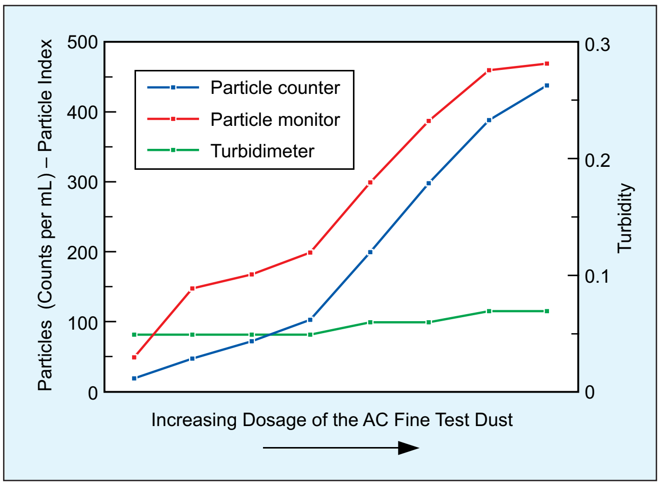

Figure 3:
Instrument comparison: particle counter, particle monitor, turbidity monitor.

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[1] AC fine test dust is a graded, naturally occurring dust frequently used as a polydisperse test aerosol. It is composed of 68 % SiO_2, 16 % Al_2O_3, and 4.6 % Fe_2O_3. The fine grade has 39 % of its mass in particles less than 5 µm in size and 73 % in particles less than 20 µm in size.

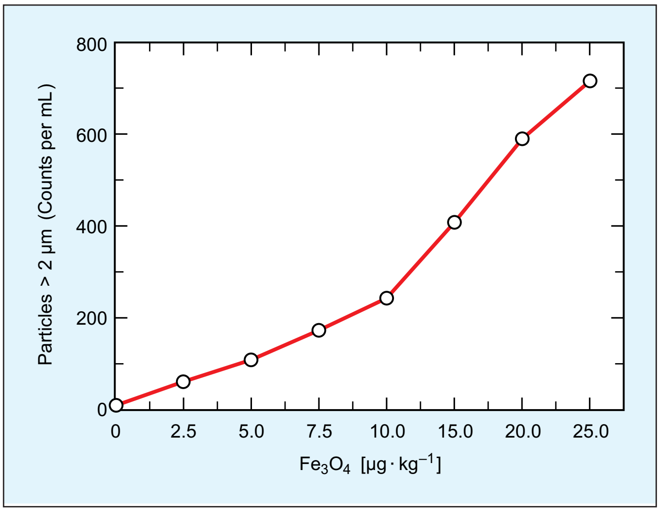

Figure 4:
Particle counter detection of Fe_3O_4 levels.

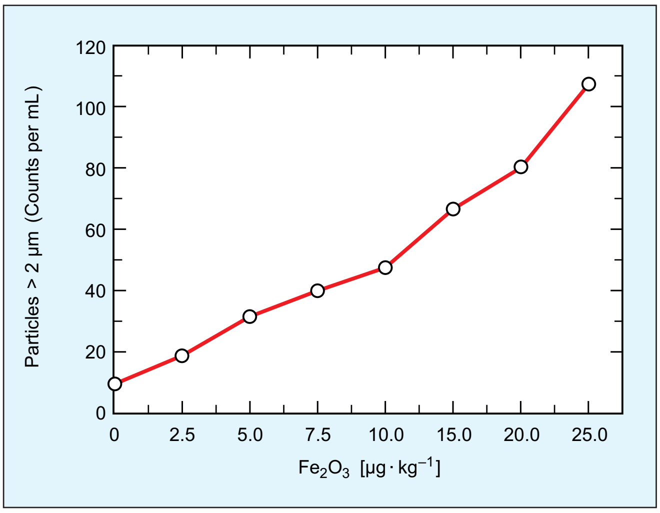

Figure 5:
Particle counter detection of Fe_2O_3 levels.

Figures 4, 5, and 6 were empirically derived using commercially available compounds of magnetite (Fe_3O_4), hematite (Fe_2O_3), and cupric oxide (CuO). A particle counter was used to size and count various concentrations of these compounds. The particle counter detects particles of 2 µm diameter and above. The lowest concentration detection limit (LCDL) is 1.0 particle in 1 mL of liquid. This calculates to 4 $ng \cdot L^{-1}$ (ppt) on a volumetric basis. Since metal oxide particles are not likely to be spherical, but more "plate-like," the mass LCDL is less than 4 $ng \cdot L^{-1}$ (ppt). Instrument response is more pronounced with magnetite than hematite. This indicates that the hematite compound has many more particles smaller than 2 µm than the magnetite.

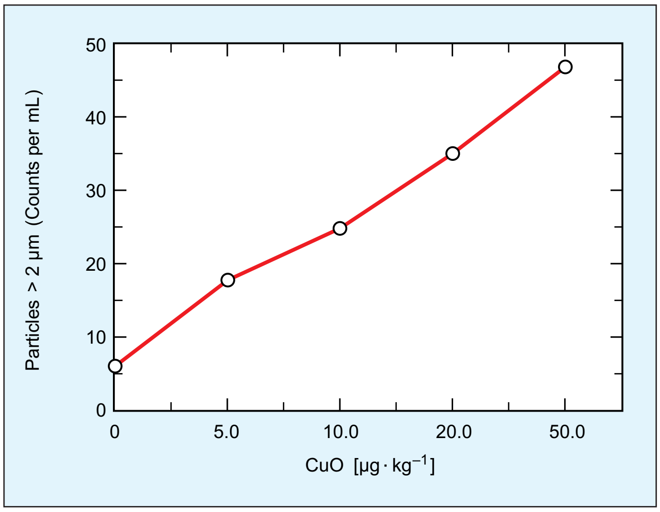

Figure 6:
Particle counter detection of CuO levels.

CURRENT STUDIES

Case histories that profile the use of particle detection instrumentation in power plants have been presented in past papers [1–4]. Topics covered have included corrosion product transport monitoring, as well as pretreatment filter optimization, steam carryover monitoring, and condenser leak detection. Current studies are focusing more on corrosion product transport monitoring.

Combined Cycle HRSG Cycling/Peaking Plant [3]

For a couple of weeks the particle counter/monitor and sampling pads indicated a very clean operation with minimal counts/particle index and very low metal analysis (less than 0.5 $\mu g \cdot kg^{-1}$). Then two "excursions" occurred that were distinct and significant. The first was a major load change that occurred on the unit (Figure 7). During the load change there was a significant increase in particle counts throughout the cycle. The boiler feedwater and condensate pump discharge samples were most affected. During this time the boiler drum pressure dropped and so did boiler drum blowdown conductivity. There was a slight increase in condensate feedwater cation conductivity as well as dissolved oxygen. These increases were not alarming, with peaks of 0.35 $\mu S \cdot cm^{-1}$ for cation conductivity and 12 $\mu g \cdot kg^{-1}$ for dissolved oxygen. In contrast, the particle counts increased significantly. The sample stream being filtered at the time was the condensate pump discharge, and it also showed high iron levels for the 24 h "composite" sampling period using the filter/ion exchange. However, the particle counter provided more detailed information in that it showed when the excursion took place, and that iron levels remained elevated for 24 h even though the load change "excursion" only lasted for about 3 h.

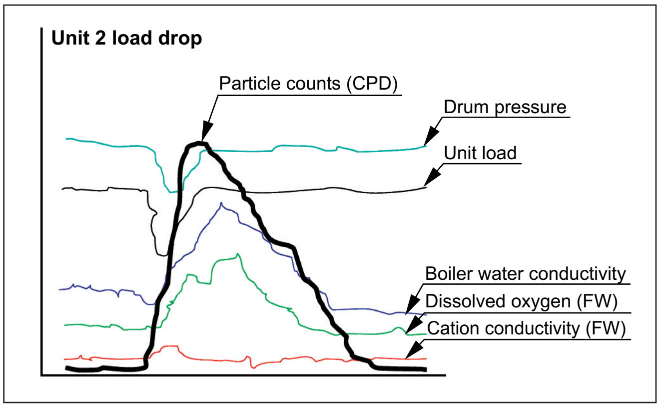

Figure 7:

Unit 2 load drop: particle counts during load change.

FW	feedwater
CPD	condensate pump discharge

Coal-Fired Power Plants A utility in the southern US has installed particle monitors in nine of their power generation units. Each one of the particle monitor systems is equipped with four sensors. So for each of the units there are four separate samples that can be simultaneously and continuously monitored. Each of the nine particle monitor systems is set-up to monitor the following samples: condensate pump discharge, condensate polisher outlet, and economizer inlet (the fourth sample that is monitored varies from location to location: boiler feed pump, main steam, heater drains, stator cooling system, etc.).

The first phase of the study will include collecting data and monitoring the particle index trends. Data evaluations will allow "baseline levels" to be established for each of the respective samples and operating ranges to be defined. This will allow "events" to be identified when some defined particle load threshold is exceeded for a predetermined period of time.

When an event takes place, data will be compared to other control parameters and system conditions in order to better understand the cause of the event. Then corrective measures will be taken and the particle index will be tracked during the recovery from the event.

Coal-Fired Plant with a Supercritical Steam Generator Another power utility in the south has installed a particle monitor in parallel with a traditional filter pad corrosion product transport monitor on a condensate sample. This allows continuous particulate monitoring and composite insoluble metals monitoring at the same time. The filter pads are removed for evaluation every two weeks. When the results from the filter pad analyses are received, the chemist is able to compare the data to the particle trends during the two-week period that the filter pad was installed.

One goal of the project is to understand the corrosion product transport relationship between the particle monitor results and the filter pad sample metals analyses. In theory, a corrosion product transport concentration estimation (in $\mu g \cdot kg^{-1}$) could be made from a correlation with the particle monitor particle index levels. Secondly, the plant will also define baseline levels, and define operating ranges for the respective sample points. Then a corrective action procedure can be established for when an event is identified.

Figure 8 shows the correlation between the particle index readings and the iron concentration in condensate.

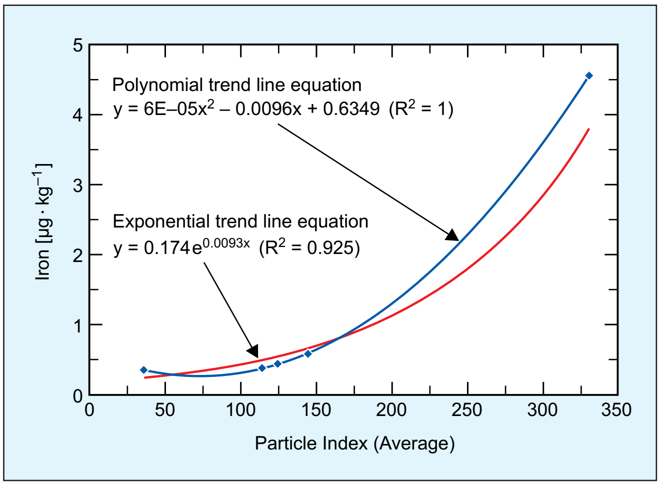

Figure 8:

Correlation between the particle index readings and the iron concentration in condensate.

Combined Cycle with an HRSG Cation conductivity, pH, oxidizing-reducing potential (ORP) and particle count (a portable particle counter) were monitored in the condensate. The data collected in a 7-day period are depicted in Figures 9 and 10. In a close cooperation with the plant personnel, the rationale for the particle count spikes will be evaluated. The spikes might be chemistry related as well as a function of operational changes (e.g., load variations).

Nuclear Plant Iron Transport Data Figure 11 shows particle counts in condensate (hotwell), polished condensate and feedwater during startup preparation (May 24) and actual startup (May 25). Please note the logarithmic y-axis scale. The data were measured in the secondary cycle of a unit with a pressurized water reactor (PWR). The monitoring results were somewhat surprising. Up to now, the corrosion product content has been exclusively measured as an average using 3-day exposed filter pads. Evaluation of the particle data recorded might help in optimizing the startup process.

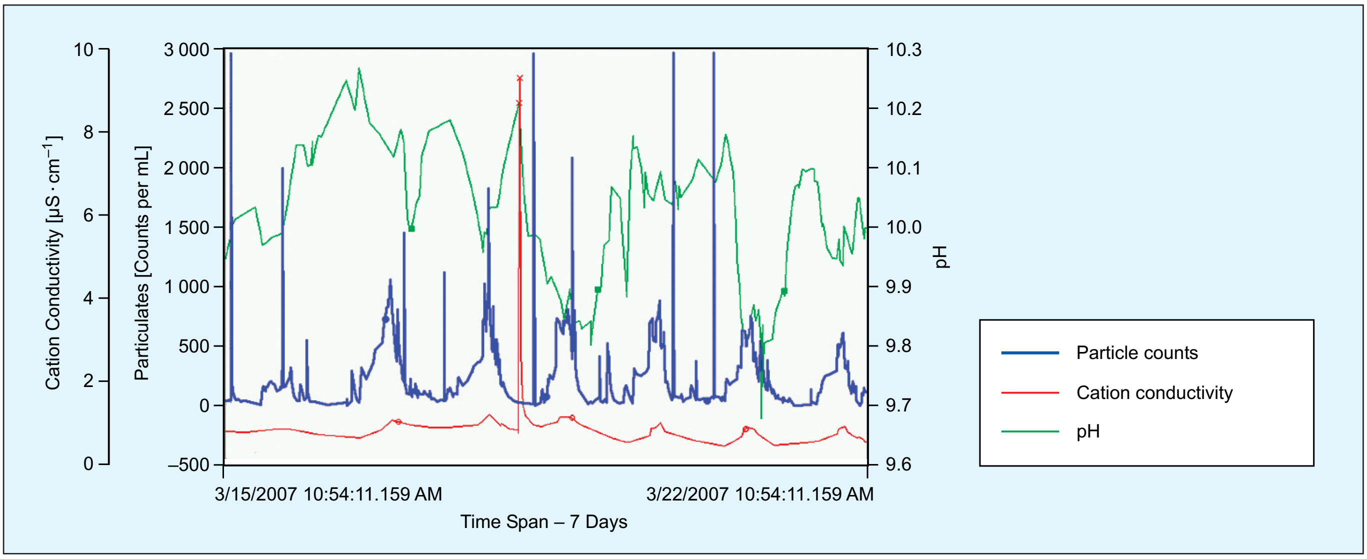

Figure 9:
Condensate in a combined cycle unit – condensate pH, cation conductivity and particle count (measured by a portable particle counter).

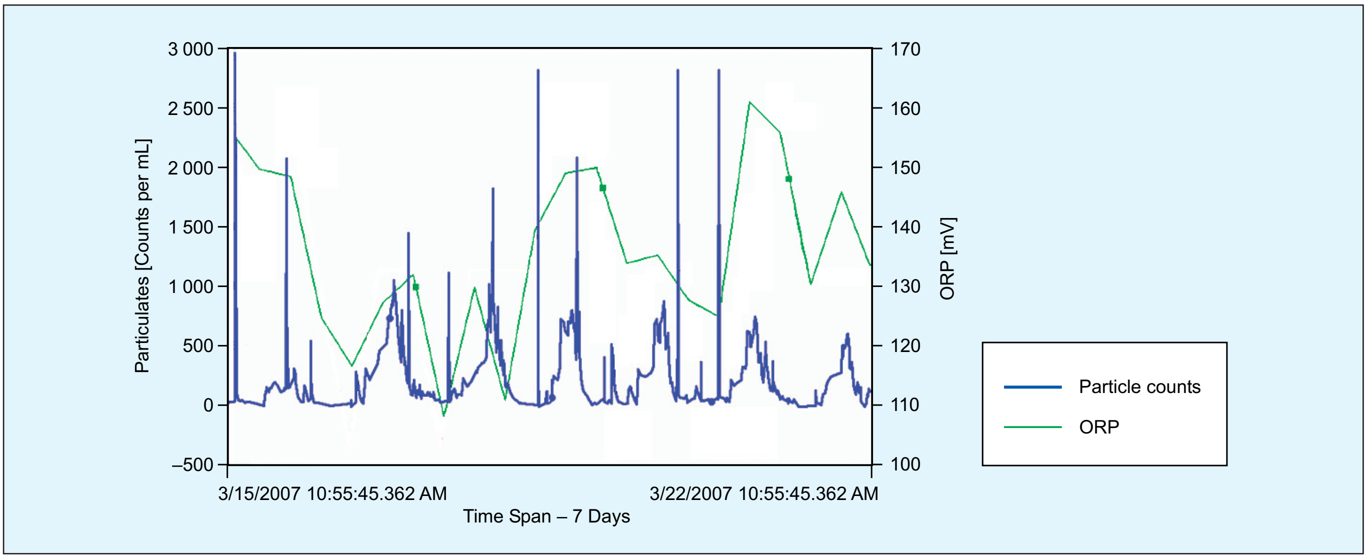

Figure 10:
Condensate in a combined cycle unit – oxidizing-reducing potential (ORP) and particle count (measured by a portable particle counter).

CONCLUSIONS

The particle monitor offers real-time online measurement of corrosion products moving through the power plant cycle. The particle monitor is not meant to replace other means of corrosion product transport monitoring, but instead to complement existing methods and offer another means of looking into the process. When combined with and compared to results from other monitoring approaches (pH, ORP, dissolved oxygen, conductivity, etc.), the plant chemist is provided with more information and can better understand what is taking place in the system.

Corrosion product transport monitoring with particle detection instruments can help identify the source of corrosion, identify when corrosion is occurring, identify how much corrosion product is moving through the system, and ultimately help minimize corrosion and control corrosion product transport.

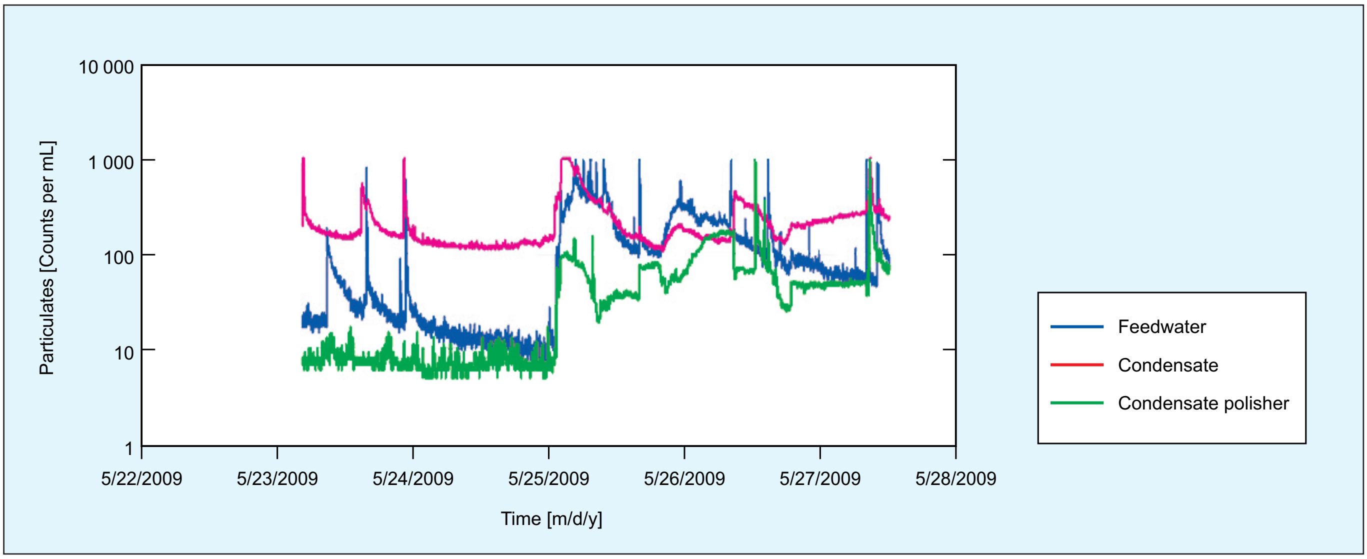

Figure 11:
Particle counts in condensate (hotwell), polished condensate and feedwater during startup of a PWR unit.

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