APPLICATION NOTE

MONITORING IRON TRANSPORT IN POWER GENERATION

Iron Corrosion and Transport

Steel piping and equipment used in the power plant steam cycle are susceptible to multiple corrosion mechanisms. Mechanical and chemical corrosion can strip and dissolve iron from steel surfaces, and this unbound iron can deposit on surfaces at other points throughout the cycle where it induces further corrosion.[1,2] Both thinning and deposition lead to equipment failure and the associated safety, cost, and productivity concerns.[3] In order to minimize the risks associated with iron transport it is essential that power generators have a reliable monitoring method. Accurate and timely analysis will facilitate informed decisions about the treatment and disposition of process streams.

Simple colorimetric lab methods have been used historically to monitor dissolved iron contamination. However, particulate or colloidal iron oxides are not detected colorimetrically without time-intensive, contamination-prone sample digestions. These oxides, magnetite and hematite, are the primary form of iron transport in both flow-accelerated corrosion and liquid drop impingement.[4,5] Detection of these species is critical for an accurate determination of iron transport. Furthermore, traditional colorimetric analyses are not capable of quantifying iron at the levels frequently sought by power generators, <2 ppb.[6]

In the absence of adequate colorimetric analytical methods, total iron determination must be performed with expensive and complicated analytical equipment. This equipment requires a very high level of expertise which makes it prohibitive for most power generators. Sample analysis for iron determination must be contracted with an outside laboratory. This eliminates the utility of the sample for timely process monitoring application. Reporting of sample data may take days or weeks, and plant processes will have changed notably during that time, rendering the sample data significantly less meaningful.

Grab Sample Total Iron Analysis

The traditional colorimetric method for dissolved iron is based on the extremely sensitive ferrozine-ferrous iron complex described by Stookey.[7] FerroZine complexes with dissolved ferrous iron to form an intense, purple-colored complex. The dissolved ferrous iron concentration may be determined by measuring the absorbance of this complex colorimetrically. Modifications of this traditional method allow for the determination of both dissolved iron and particulate iron oxides at very low concentrations.

Particulate and colloidal iron may be monitored with a surrogate technique (see below), but a total iron analysis is necessary for measuring particulate as well as dissolved iron. Flow-accelerated corrosion proceeds through the reduction and dissolution of a protective magnetite boundary layer into the bulk stream flow. The majority of this ferrous iron is re-oxidized and present as particulate magnetite, but the mechanism for this transformation is unclear.[4] As dissolved ferrous iron is known to exist as a corrosion product, and its oxidation mechanism is unknown, it is prudent to monitor this form as well as the oxidized form.

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The conventional Hach colorimetric dissolved iron procedure was modified to provide a solution for this application. The new ultra low range (ULR) procedure is capable of quantifying 1 ppb total iron with a simple 30-minute digestion. Suspended and dissolved iron are digested and reduced to the ferrous state using Hach FerroZine reagent and the Hach DRB200 digestion block. Ferrous iron complexes with the same FerroZine reagent to produce a purple-colored complex which may be analyzed colorimetrically. The intensity of the FerroZine-iron complex is directly proportional to the total iron concentration of the sample. The low detection limit is achieved through the use of a stable PourThru/Sipper Cell apparatus with a Hach DR6000 or DR3900 spectrophotometer.

Figure 1: Combination reagent, sample/digestion vials, and digestion block



Low level analyses using any technique can be extremely difficult due to the possibility of sample contamination and the precise analytical technique required to obtain repeatable results. The Hach ULR Total Iron Analysis minimizes contamination via simplified procedures, minimal reagent use, and minimal sample manipulation. The use of a combined reagent limits the opportunity for sample contamination by minimizing sample exposure, as does the use of a combined sampling-digestion vial. The sample is taken directly into the DRB200 digestion vial. FerroZine reagent is added. The vial is capped and digested. The digested sample is sipped or poured into the sample cell and read. With careful technique, a simple, inexpensive, and timely ULR total iron determination can be performed in the typical power plant laboratory.

Figure 2: Sipper cell for improved sensitivity



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Real-Time Surrogate Monitoring

Iron transport as iron oxides may be monitored in real time by a surrogate technique. As the process waters used in power generation are particularly pure, it can be assumed that any insoluble matter present in a ferrous metallurgy process stream is particulate or colloidal iron oxide. Particle monitoring and nephelometry (turbidimetry) instruments have been used successfully to monitor iron transport.[8,9]

The obvious advantage of surrogate monitoring techniques is the ability to track transport events in real time. This has led to the observation that the majority of these events occur during system cycling.[8] This type of information is impossible to obtain using grab sample analyses. And it can have profound effects on the generator's ability to make informed decisions concerning treatment or disposition options.

While particle counters, particle monitors and nephelometers are capable of detecting particulate iron transport, the nephelometer enjoys several advantages over the particle counter and monitor. The nephelometer is easily calibrated, and may be used to determine absolute iron oxide concentrations.[9] The nephelometer, particularly with a laser light source, is also significantly more sensitive than standard particle counting or particle monitoring techniques, which do not detect particles less than 2 µm.[10]

Figure 3: Laser Nephelometer



Hach laser nephelometers have been in use in the water industry for more than a decade and their primary application is in the monitoring of filter effluent.[11] The FilterTrak 660 light source is a 660-nm laser diode that projects a collimated beam through the sample stream. Particulate material that is within the sample will scatter the beam in all directions. A detector is positioned at a 90-degree angle to the incident light beam to detect this scatter. Scattered light that reaches this detector is then converted to a signal that is scaled to a common calibration standard for turbidity. The TU5400 laser nephelometer uses a 650-nm light source, and measures scattered light collected from 360 degrees around the 90-degree incident axis.

Figure 5 summarizes the correlation between magnetite iron, expressed as total iron, and turbidity for both laser nephelometers. The graph shows a highly linear correlation as is typical for nephelometric calibrations.

Figure 4: TU5400 Laser Nephelometer



Similar correlations have been derived for hematite and for the 50:50 mass fraction of hematite-magnetite. The responses to hematite are three times greater than magnetite, and the 50:50 mass fraction spikes have a response between the two separate correlation curves. This difference is due to the relative absorbance characteristics of the different oxides. The black magnetite will absorb significantly more of the incident light from the turbidimeter, resulting in a reduced response. The red hematite has lower absorbance characteristics which allows for more efficient light scatter from its surface, producing a higher turbidimetric response.

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Figure 5: Magnetite Calibration Curve

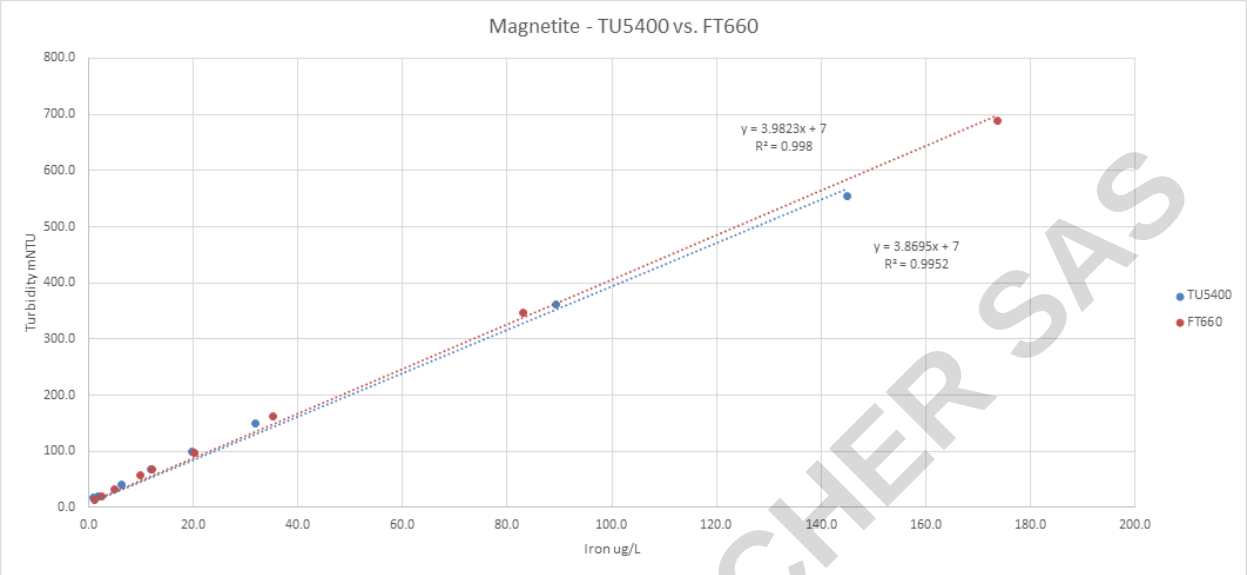
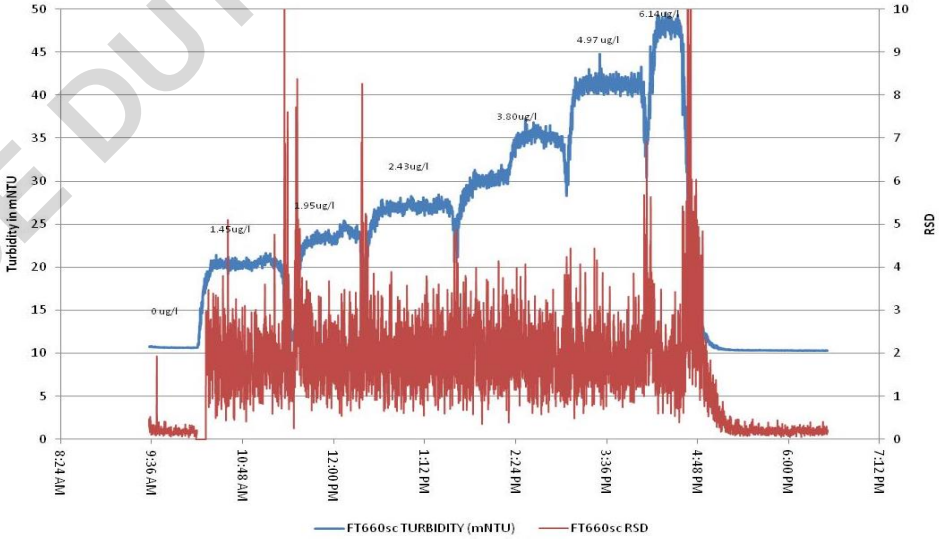


Figure 6 shows a typical response curve for the laser nephelometer through the different levels of particulate iron. The blue trace is the turbidity measurement at several different levels of particulate iron. The numerical values above this trace indicate the different concentrations of particulate iron injected. The red trace is the instrument relative standard deviation (RSD) parameter. This parameter is a measurement of the degree of variability of the measurement baseline. A low RSD value, anything below 0.5, is indicative of a particle-free baseline, and anything above this value is indicative of the presence of particles.[12] The RSD value is a confirmative response to the elevated turbidity values that result from the particulate iron. The RSD parameter may be used as a leading indicator of iron transport as it is sensitive to the leading edge of any slug transport.

Figure 6: Turbidimeter Spike Response



Establishing an Effective Iron Transport Monitoring Program

An effective iron transport monitoring program requires accurate, timely, reliable analytical methodology coupled with judicious choices of monitoring location and frequency. Startup and shutdown operations typically initiate the largest transport events. These transient events cannot be easily tracked with grab sampling and require on-

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line monitoring. Additionally, feed water purity must be determined with a direct iron analysis and cannot be monitored via a surrogate method as there is no baseline available for reference. Both grab sampling and process monitoring must be employed for a complete iron transport monitoring program.

Real-time monitoring of iron transport may be accomplished with a Hach TU5400 or Hach FilterTrak 660 laser nephelometer. One unit may be placed in the demineralized water feed line to establish a baseline turbidity of the process water. A second nephelometer should be placed in the condensate return line to monitor iron transport for the entire steam cycle. Additional nephelometers may be placed at other points of interest throughout the process. Comparison of the process turbidities to the feed turbidity will allow for real-time monitoring of iron transport events associated with each individual unit operation.

Grab samples for total iron determination may be analyzed with Hach spectrophotometers and cells. Grab sampling should be performed on the demineralized feed water to ensure that feed water is iron-free. Grab samples may also be taken after any unit operation, and particularly from the condensate return. For the most accurate data, samples should be taken with an isokinetic sampler. If isokinetic sampling is not possible, sample lines should be thoroughly flushed prior to each sample collection in order to ensure that grab samples are representative of process streams.

Hach Iron Transport Monitoring Solutions

Nephelometric Particulate Iron Process Monitoring

- TU5400 sc Laser Nephelometer - PN LXV445.99.10212
- FilterTrak 660 sc Laser Nephelometer Sensor – PN 6016000
- SC200 or SC1000 Controller – SC1000 allows for display in µg/L iron

Colorimetric Total Iron Grab Sample Analysis

- DR6000 or DR3900 Spectrophotometer – PN LPV441 or LPV440
- DRB200 Digital Reactor Block – PN DRB200
- FerroZine Iron Reagent Solution – PN 230149
- 20-mm Digestion Vials – PN LZP065
- PourThru Cell Kit or Sipper Cell Kit – PN LZV889, LQV157.99.20002, or LQV157.99.10002
- 59 mL Dropping Bottle – PN 2937606
- 1 mg/L Iron Standard – PN 13949
- Variable Volume Pipettes – PN LZP320
- Deionized Water – PN 27256
- 6N Hydrochloric Acid – PN 88449

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