

Monitoring Iron Transport in the Steam Cycle via Grab Sample and Online Methods

Abstract

Quantitative online monitoring of iron corrosion product transport is an ongoing technical challenge. Total iron measurements require digestion of the particulate and colloidal iron oxides which constitute the majority of these products. Particle monitoring is fast and simple, but is not quantitative.

The present study combines a modified total iron analysis with a laser nephelometer to create a quantitative online monitoring system. This system is applicable in the steady-state flow regime where flow corrosion products are consistent. The calibration is specific to the particular corrosion product characteristics present at the individual nephelometer installation site.

Introduction

Corrosion of ferrous steam cycle components is a serious safety and financial risk with potential to cause fatal accidents, significant repair costs, and lengthy downtime.⁽¹⁾ Accordingly, monitoring iron corrosion is a high priority for power generators. Total iron monitoring has historically been performed via grab sampling and expensive, time-intensive laboratory analysis.⁽²⁾ Since iron corrosion exists primarily in particulate or colloidal form, online monitoring using nephelometers and particle analyzers have been employed as surrogate measurement techniques.^(3,4) These kinds of instruments provide real-time data, but they do not measure iron directly, and they do not offer quantitative iron concentrations.

A combination of a simple colorimetric total iron laboratory analysis with a sensitive nephelometric analyzer can provide a solution for cost effective, quantitative, real-time corrosion monitoring. When properly calibrated, the nephelometric units provided by a nephelometer can be correlated to total iron concentration values. The iron concentration of the process water is a direct indicator of steel corrosion.

Background

As the process waters used in power generation are extremely pure, it can be assumed that almost all insoluble matter present in a ferrous metallurgy process stream is due to steel corrosion in the form of particulate or colloidal iron oxides. Corrosion of steel components in power generation is generally found as iron oxides and hydroxides, primarily, iron(II,III) oxide (magnetite), α -iron(III) oxide (hematite), or dissolved iron.⁽¹⁾ Each of these species produces a different nephelometric response to visible light. Black magnetite absorbs more and reflects less light than red hematite. Dissolved iron does not produce any nephelometric response.

Corrosion products range in size from sub-micron to 10 μm in diameter, with an average diameter of 1 μm .⁽⁵⁾ This range of diameters poses another challenge for particle monitoring because nephelometers respond differently to different particle sizes.

The variables associated with iron corrosion products (species, color, particle size) make it impossible to create a universal nephelometric calibration for quantification of corrosion products. A nephelometric calibration which is appropriate for a particular sample location with particular corrosion characteristics will not be accurate for a different location with different corrosion characteristics. For instance, 5 $\mu\text{g/L}$ of iron present as 1 μm hematite particles might produce a nephelometric response of 70 mNTU. A concentration of 10 $\mu\text{g/L}$ iron present as 3 μm magnetite might produce the same 70 mNTU nephelometric response. A nephelometer calibrated with 1 μm hematite, but installed at a location where corrosion was present as 3 μm magnetite, would under report the iron

concentration by 50% at 70 mNTU. This simple example could be complicated significantly if the iron present at each location were assumed to be a mixture of species at variable particle sizes, as is expected in real-life applications.

Quantification of total iron via nephelometry must be accomplished through site-specific calibration. Variability in water chemistry, phase, and local piping configurations contribute to variable corrosion characteristics. Site-specific calibration ensures that nephelometric response is correlated to the specific corrosion characteristics present at each installation.

The local corrosion environment operates close to a steady-state provided that the water chemistry is not changed.⁽⁵⁾ This steady-state environment allows for accurate calibration of turbidity with those corrosion products produced by steady-state flow induced corrosion mechanisms such as flow accelerated corrosion (FAC).

While this kind of calibration technique can be useful for quantitatively monitoring steady-state corrosion product transport, it will not provide accurate quantitation of those transient transport events which are characteristic of transport during start-up, shut-down, or cycling operations. Transient slugs of very high concentrations of corrosion products have been observed during these operations.⁽⁶⁾ As these slugs are related to different corrosion mechanisms than those responsible for steady-state corrosion, the corrosion product characteristics (species, color, size) of the slug will not match those used for the calibration. Hence, while the calibrated nephelometer will produce quantitative iron concentration values during one of these transient events, these values can only serve as an estimate of the true concentration. Techniques for quantifying these events are discussed elsewhere.⁽⁷⁾

Site-specific calibration requires on-site total iron determination. Modifications to the traditional Hach® FerroZine ferrous iron analysis have made this technique suitable for this application.⁽⁸⁾ This procedure is faster, simpler, and less expensive than other analytical techniques historically used to quantify low concentrations of iron oxides. The digestion recovers all of the relevant iron species, dissolved, magnetite, and hematite. The quantitative range of the modified procedure encompasses the concentrations relevant to iron corrosion transport monitoring, 0.7 to 100 µg/L.

The current study combines the online nephelometric analyzer with the modified total iron analysis to create a simple, quantitative, site-specific calibration for iron corrosion product monitoring. Grab samples taken from the nephelometer are analyzed with the total iron lab procedure, and the nephelometric values for each sample correlated with the measured total iron concentration. This calibration provides accurate, quantitative real-time monitoring of corrosion transport.

Methods and Materials

Calibration curves were generated for various commercially available oxides. Suspensions of these oxides were prepared by adding the powdered oxide to a measured volume of 0.01M HCl. The suspension was constantly vigorously stirred with an IKA overhead stirrer. The suspension was also constantly ultrasonicated in a Branson ultrasonic bath. This combination of vigorous stirring and ultrasonication produced a uniform suspension suitable for extended periods of testing (see Figure 1). Magnetite and hematite, <5 µm, were purchased from Sigma-Aldrich. Magnetite and hematite, nano-powder, were purchased from Alfa Aesar.

The oxide suspensions were pumped into the inlet streams of a Hach TU5400 and FT660 laser nephelometers. Filtered deionized water at 200 mL/min was used as the makeup flow. Turbidity values were recorded with a Hach SC200 controller.



Figure 1: Particulate Hematite Suspension

Grab samples were taken from the outlet of the nephelometer. Grab samples were analyzed on a Hach DR3900 spectrophotometer using Hach Method 10263, and Hach FerroZine reagent.

Site-specific calibration curves were generated with the same equipment at a base-load, coal-fired generating plant. An FT660 with SC200 controller was installed on the condensate return line. Samples were taken when the turbidity values had been steady for at least 30 minutes.

Turbidity was correlated to measured iron concentrations by averaging the milli-nephelometric turbidity units (mNTU) from the 10 minutes prior to the sample time. The “Bubble Reject” function was activated. Signal averaging was set to 6 seconds, with a data log interval of 30 seconds.

Results and Discussion

Turbidity versus iron concentration plots were created with $<5\ \mu\text{m}$ hematite, $<5\ \mu\text{m}$ magnetite, and nano-magnetite (50-100 nm). The different nephelometric responses to the characteristics of each oxide are evident in the slopes of the associated trendlines. Figure 2 shows the response difference due to the colors of magnetite and hematite for both laser nephelometers. The slope of the red hematite curve is approximately three times steeper than that of the black magnetite. The nephelometer will be more sensitive to hematite as a result. Due to the TU5400 measurement system, it is much more sensitive to hematite than the FT660. Magnetite gives the same response for both nephelometers.

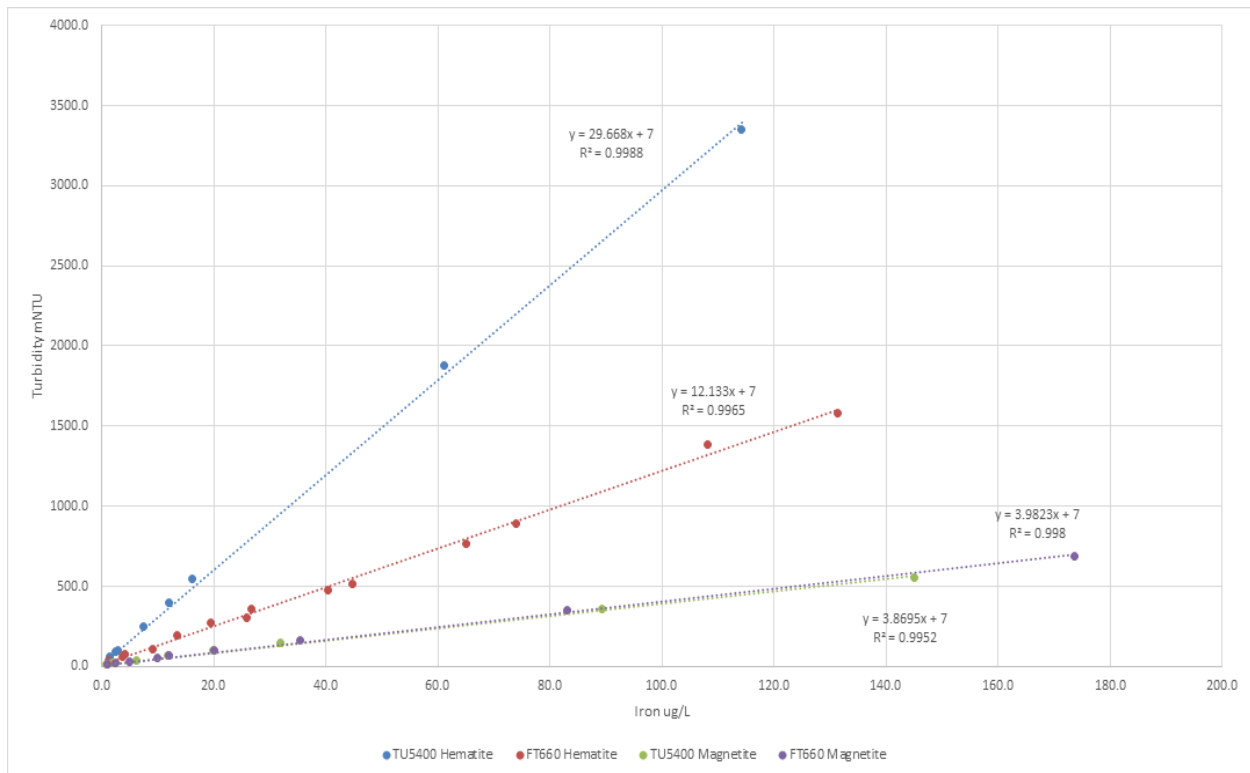


Figure 2: $<5\ \mu\text{m}$ Oxide Calibration Curves

Figure 3 shows the FT660 response curve for nano-magnetite. This curve demonstrates the suitability of the nephelometer to monitoring for this application. Very low concentrations of black particulates should be the most difficult to detect for a nephelometer. But the response curve for these particles is linear and distinct from the baseline turbidity even in the single digit $\mu\text{g/L}$ range.

These plots also illustrate the excellent linearity of nephelometric calibrations. This is a characteristic of the technology, and is advantageous for creating calibration curves. The entire calibration curve can be generated with two data points. With a known intercept, a calibration curve can be generated from a single data point. This kind of single-point calibration is common in drinking water applications.

These curves were all forced through the empirical zero point of contaminant-free water. Even water which is completely free of particulates will generate a non-zero turbidity value. In-house testing of the TU5400 and FT660 has determined that the empirical zero value is 7 mNTU for these nephelometers. Single-point calibration is necessary for this application. Since the calibration is dependent upon the specific corrosion products at each nephelometer installation, a synthetic calibration standard cannot be made. The only data suitable for the calibration are those points found during steady-state operation. And as the steady-state turbidity does not vary significantly, there are not adequate data to construct a multi-point calibration.

The empirical 7 mNTU intercept was used to generate several site-specific linear calibration curves with a single iron concentration measurement. These curves account for the specific corrosion characteristics present in the process stream (condensate return). Four curves were created from grab samples taken over a 24-hour period. Steady-state turbidity values remained between 22-32 mNTU during this period. The single-point data and curves are shown in Table 1.

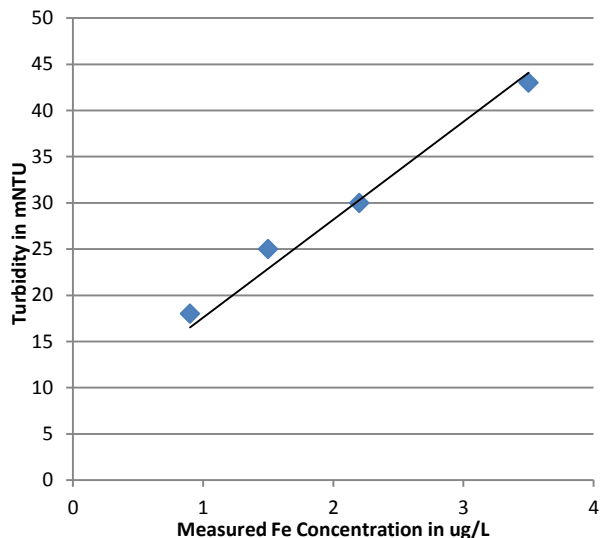


Figure 3: Nano-Magnetite Low Range Curve

Table 1 – Site-Specific Calibration Data

Average Turbidity (mNTU)	Average Iron (µg/L)	Slope	Intercept
24.6	2.6	6.77	7.0
24.3	2.3	7.52	7.0
29.1	3.0	7.37	7.0
25.6	2.4	7.75	7.0

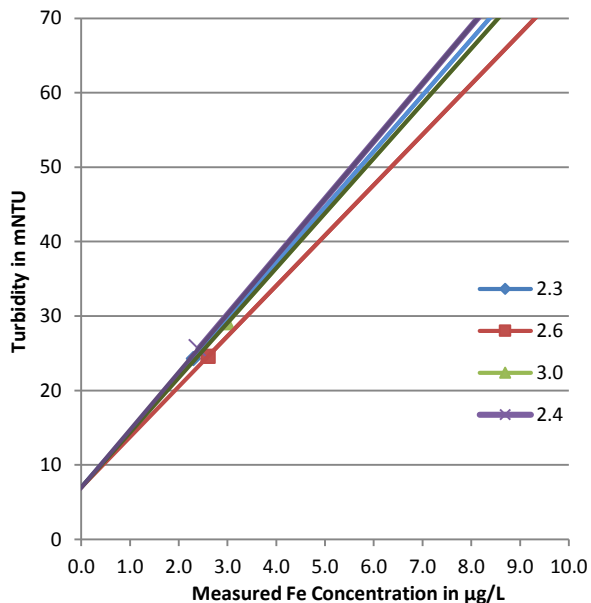


Figure 4: Site-Specific Calibration Curves

A concern when creating single-point calibrations is the potential for a non-representative data point to bias the entire curve. The similarities in the slopes of the curves in Figure 4 illustrate that this concern is minimal for this application. While good analytical and sampling techniques are required to achieve these results, the data indicate that this approach is reasonable over a limited range. Over the range of turbidity values measured during this study, all of the curves agreed within an absolute concentration of 0.4 µg/L iron. The calibrated iron values agree within 1.0 µg/L iron between all curves through 60 mNTU. At this turbidity the “2.6” curve produced a concentration of 7.8 µg/L iron and the “2.4” curve produced a concentration of 6.8 µg/L iron. Each of the individual slopes shows >90% agreement with the average slope.



While this agreement extends throughout the entire curve, it is not recommended that values $>5 \mu\text{g/L}$ of the calibration point concentration be considered accurate. If a steady-state turbidity baseline is observed at a higher value than that used to generate the original calibration curve, a new curve should be determined. A baseline change of this kind may indicate a change in the corrosion environment, and any change in corrosion product characteristics would necessitate a new calibration.

Conclusion

The presence of iron corrosion as particulate oxides is advantageous for online corrosion product transport monitoring. Monitoring via nephelometry is extremely fast, generating real-time data without the lag time associated with batch analyzers.

Particulate and colloidal iron oxides can be monitored quantitatively at very low concentrations via nephelometry. A site-specific calibration of turbidity with total iron concentration will yield accurate iron concentration data for the steady-state operating regime. The modified FerroZine procedure can be used to perform this simple single-point calibration. The combination of nephelometer and FerroZine lab analysis create a powerful solution for iron corrosion transport monitoring.

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