

Further Advances in Monitoring Low Level Iron in the Steam Cycle

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Abstract

In an earlier paper, it was discussed how a laser Nephelometer could be used to detect the transfer of corrosion products in a HRSG power plant at ppb levels with particles in the sub-micron size range. Also, a modified trace level iron test was documented using colorimetric methods on a lab spectrophotometer to measure total iron levels to 1ppb.

In this paper, further advances will be outlined which improve the accuracy and repeatability of the lab method, while providing further insight into the level of protection being provided to steam cycle components against FAC and other corrosion mechanisms. Focus will be in understanding the chemistry of the measurement so as to provide more specific data to plant personnel regarding the level and species of iron being observed.

Background and History

The traditional colorimetric method for dissolved iron is based on the extremely sensitive ferrozine ferrous iron complex described by Stookey (1). Ferrozine complexes with dissolved ferrous iron to form an intensely colored purple 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 surrogate techniques, 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 (2). 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.

The reductive dissolution of iron oxides via thiol-containing compounds has been thoroughly investigated by Waite et al. Thioglycolic acid (TGA) has been used to successfully dissolve and reduce various iron oxides. While magnetite is dissolved relatively easily with TGA, hematite has been shown to be much more resistant to this method (3, 4). However, TGA is compatible with the sensitive ferrozine reagent and is commercially available as a combined reagent. This combination digestion-reduction-detection reagent is particularly useful for simplifying analysis and minimizing contamination.



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

Complete dissolution of particulate magnetite and hematite was shown to be achieved with a 150°C, 30 min closed vessel digestion using 300 µL of combination reagent and 15 mL of sample. The digestion is carried out in a 20 mL glass vial heated in an aluminum block (Figure 1). After the sample has cooled the absorbance is read with a spectrophotometer by using either a 10 cm cell or the pour-thru or sipper methods of feeding sample (Figure 2). The calibrated range using this procedure is 1-100 µg/L with a method detection limit (MDL) of 0.3 µg/L.

Iron Speciation

The current study takes advantage of the different dissolution rates of magnetite and hematite in this highly controlled analytical environment. Using three identical samples and three different reaction conditions, it is possible to determine the amount of each species present in the bulk sample. The extent of dissolution of each oxide under various reaction conditions was determined empirically. A simple algebraic formula was then created from these data to calculate the concentrations of each species. This technique assumes that only hematite, magnetite, and dissolved iron species are present. Commercially produced hematite (<5 µm) and magnetite (<5 µm) were utilized for the testing along with the following: FerroZine reagent, dissolved iron standard, DR6000 spectrophotometer, DRB200 digestion block and vials.



Figure 2: Spectrophotometer with sipper cel

Suspensions of hematite particles were prepared by adding hematite powder directly into a measured volume of 0.01M HCl during vigorous overhead stirring. Suspensions of magnetite were prepared by ultrasonication in 0.01M HCl. Aliquots of these suspensions were taken into the digestion vials during stirring or ultrasonication. The digestion vials were then brought to a volume of 15 mL with DI water. The total iron concentration of each preparation was determined with the total iron reaction conditions. Percent recoveries were calculated against this determined concentration.

Data & Results

Magnetite was digested at 50, 70 and 150°C. It was completely dissolved (>95.0% recovery) under all reaction conditions within 25 minutes. Hematite was digested at 150°C, and had completely dissolved within 15 minutes at this temperature (Figure 3).

Four digestions of eight replicates of hematite were digested at 50°C. The percent recoveries for these replicates ranged from 9.8-11.2%, with an average of 10.6% (Figure 4).

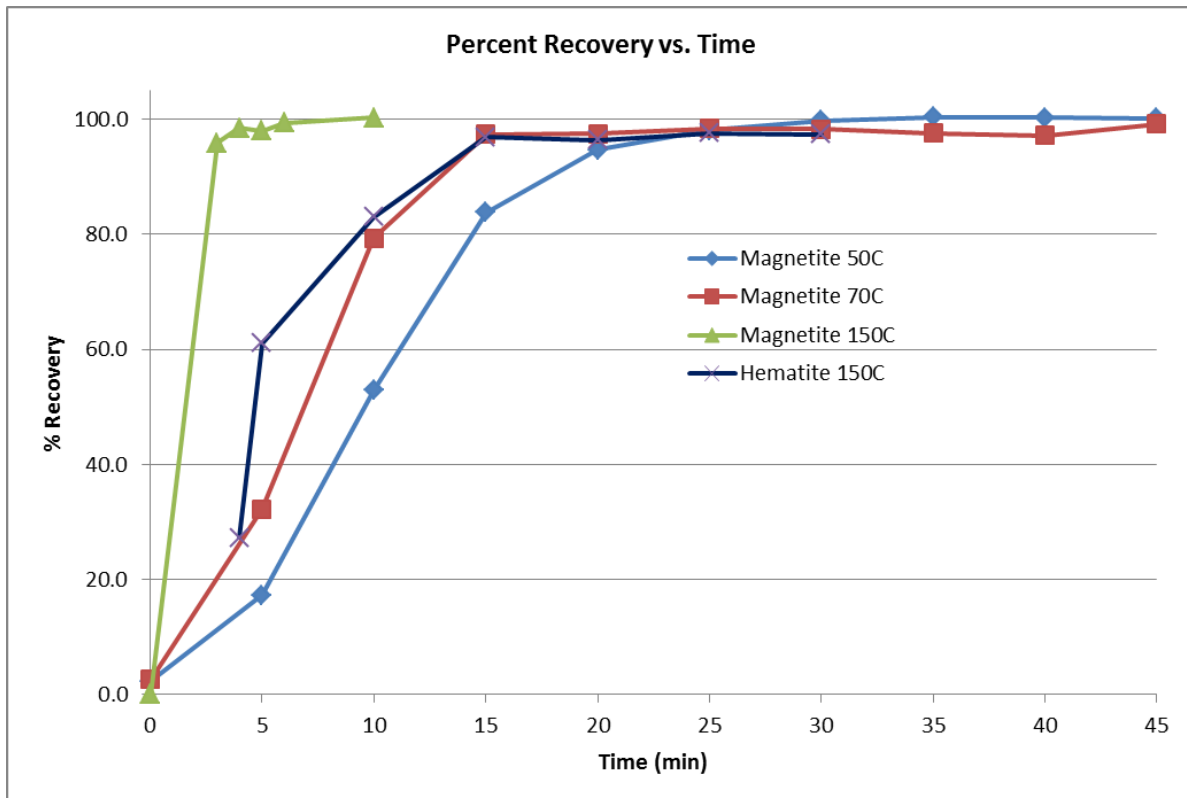


Figure 3

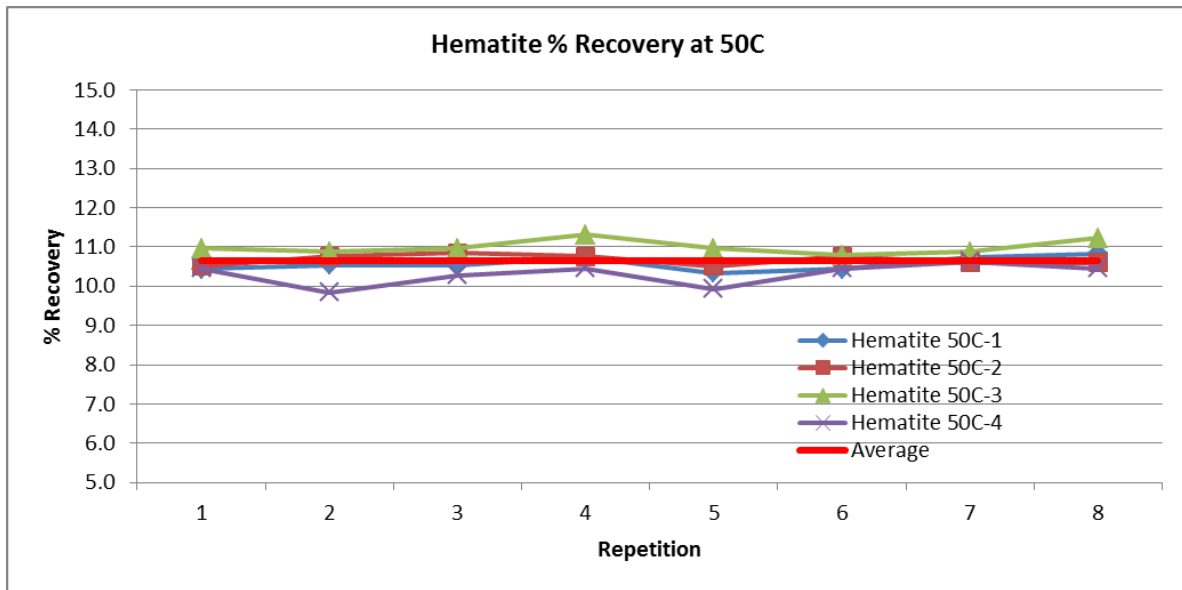


Figure 4

Calculations

These data allow for the calculation of each iron species. Dissolved iron is determined in one digestion vial with a 3 minute, room temperature reaction. Dissolved iron, magnetite, and 10.6% of hematite are determined in a second digestion vial with a 30 minute, 50°C reaction. Total iron is determined in a third digestion vial with a 30 minute, 150°C reaction. The concentration of each oxide can be calculated using the following equations.

$[50C] \equiv$ determined value from the 50C digestion

$[T] \equiv$ determined value from the 150C digestion

$[D] \equiv$ determined dissolved iron concentration

$[M] \equiv$ magnetite concentration

$[H] \equiv$ hematite concentration

$$[T] = [M] + [H] + [D]$$

$$[50C] = [D] + [M] + 0.106[H]$$

$$[H] = \frac{[50C] - [D] - [M]}{0.106}$$

$$[T] = [M] + [D] + \frac{[50C] - [D] - [M]}{0.106}$$

$$\text{Total Magnetite} \Rightarrow [M] = \frac{[50C] - 0.106[T]}{0.894} - [D]$$

$$\text{Total Hematite} \Rightarrow [H] = [T] - \left(\frac{[50C] - 0.106[T]}{0.894} \right)$$

Sampling

The International Association for the Properties of Water and Steam (IAPWS) offers some good guidelines to assure that a representative iron sample is being collected (5). The optimum place to sample for corrosion products is from a stream that has moderate to high velocity, is downstream, and as close as possible to the component of interest in the loop. While sampling can be done in a number of locations, the most beneficial are summarized below (Figure 5).

Sampling Locations	Plant Type	
	Fossil - All Ferrous	CC / HRSG
Condensate Pump Discharge	X	X
LP & HP Heater Drains	X	
Economizer Inlet	X	X
Boiler / Evaporator		X
* ACC Outlet	X	X
* Condensate Filter Outlet	X	X

* if ACC or Condensate Filter installed

Figure 5

It is important to have a good degree of turbulence present in order to insure a representative sample of total iron. A Reynolds number of greater than 2300 in a straight section of pipe will ensure good turbulence throughout the loop. Where one does not have much control over the existing design, samples should only be collected after running the line for at least 2 hours at a linear flow velocity of 1.9 m/sec or at the highest rate possible. Ideally sample lines and isolation valves should be constructed of 316L stainless steel.

While sample location and line construction are critical parameters in the sampling process, the operator often has limited control over these factors in an existing plant. On the other hand, sampling technique is an equally important parameter, and one which the operator can significantly impact, even in an older facility.

From an appropriate sampling location, samples must be collected in acid-washed glass or plastic bottles. The glass bottles can be cleaned prior to sampling with a 1:1 hydrochloric acid solution. It is important to rinse the bottles well with DI water after cleaning. A minimum sample size of 100ml should be collected from each location desired.

Another option is to sample directly into the digestion vials. This technique may prove to be more convenient for the operator or technician collecting the sample. The direct method would also be less prone to contamination while eliminating the concern with materials adhering to the inner surface of the sample container.

Once the digestion is complete, the samples should be allowed to cool. The digested sample can then be analyzed, when it is convenient, up to several hours later.

Conclusions

Improvements to the Ferrozine Method of analyzing total iron have now been made, bringing sensitivity down to the 1ppb level. By altering the digestion process, it is now possible to differentiate between the hematite and magnetite forms of iron in the sample.

Even with improved analytic capabilities, sampling remains a concern and an area that needs attention. Drawing samples at strategic locations in the loop will help insure that the readings alert the operator to potential concerns within the system. Yet for those samples to be representative, flows and linear velocities within the pipe need to be selected that keep iron particles suspended. Good laboratory techniques will further insure that the sample taken is not contaminated or altered in the analytical portion of the measurement.

References

1. Stookey, L. "Ferrozine-A New Spectrophotometric Reagent for Iron." *Analytical Chemistry*. 1970, 42(7), pp.779-781.
2. Dooley, R. B. "Flow-Accelerated Corrosion in Fossil and Combined Cycle/HRSG Plants." *PowerPlant Chemistry*. 2008, 10(2), pp. 68-89.
3. Waite, T. D., Torikov, A., Smith, J. D. "Photoassisted Dissolution of Colloidal Iron Oxides by Thiol Containing Compounds." *J. Colloid and Interface Science*. 1986, 112(2), pp. 412-420.
4. Baumgartner, E., Blesa, M., Maroto, A. J. G., "Kinetics of the Dissolution of Magnetite in Thioglycolic Acid Solutions." *J. Chem. Soc. Dalton Trans*. 1982, 1649-1654.
5. IAPWS, Technical Guidance Document: Corrosion Product Sampling and Analysis for Fossil and Combined Cycle Plants (2013). Available from <http://www.iapws.org>

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