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Qualitative corrosion monitoring by on-line ion chromatography

Dennis Bostic

Virginia Electric and Power Co., Surry Power Station, P.O. Box 315, Surry, VA 23883 (USA)

Gary Burns

GEBCO Engineering Inc., 138 N. Main St., Suite 36, Sebastopol, CA 95472 (USA)

Sam Harvey*

Tennessee Valley Authority, 1101 Market St., Chattanooga, TN 37402 (USA)

ABSTRACT

The corrosion mechanism for secondary side systems of pressurized water reactors has always been difficult to monitor and quantify. Ion chromatography may be the method to evaluate the corrosion phenomena using on-line systems.

Two separate ion chromatography methods have been developed to monitor manganese, a component of carbon steel and stainless steel used in secondary system piping. The first method employs step gradient cation-exchange separation with chemically suppressed conductometric detection. The second method employs traditional transition metal analysis using an analytical column followed by post-column reagent addition and mixing with visible detection at 520 nm.

The presence of manganese was verified using corrosion product monitors. Each monitor has a 0.45- μm particulate filter followed by three cation-exchange membrane filters for the determination of soluble metallic species. Atomic absorption spectrophotometry was employed to analyze the processed filters.

Results for the corrosion monitors and the ion chromatography methods were compared to attempt validation of all methods and to establish practical methods for on-line corrosion monitoring.

INTRODUCTION

In the nuclear industry an understanding of the mechanisms and rate of corrosion is required to maximize plant reliability and minimize operational costs. In addition this is necessary to fulfill the utilities' obligation to the general public for safe operation of the plant.

Evaluation of corrosion processes in domestic nuclear plants requires an understanding of the plants operational parameters. Boiling water reactors (BWRs) boil water surrounding the uranium core to form steam that drives the turbines and electrical generator. Condensed steam is returned to the system, and as a result of this recycling, non-

volatile anionic and cationic impurities concentrate in the reactor and recirculation water. Other impurities are introduced into the cycle by corrosion of metal surfaces; this corrosion is minimized by maintaining feedwater dissolved oxygen at 20–50 ng/ml. Metallic corrosion impurities can deposit on core surfaces, and become radioactive via neutron activation. Heavy corrosion deposits on the fuel can cause cladding failures and release radioactive fission products into the coolant. Corrosion impurities adhering to core surfaces and other metal surfaces are slowly released during steady-state operation, but can be rapidly released during large power transients or from significant changes in system chemistry. The radioactive deposits not only affect

heat transfer efficiency but are also a potential radiological hazard to personnel performing maintenance and testing.

Pressurized water reactor (PWR) plants have a primary loop of water circulating through the nuclear core in a system under 2250 p.s.i. pressure and at 296°C without boiling. In a secondary loop treated water is circulated through large heat exchangers, called steam generators, where heat is removed from the primary loop, causing the secondary water to become steam, which drives the turbine and electric generator. Because many construction metals are used in the secondary loop, the secondary water must be ultrapure and treated to minimize corrosion. Corrosion products, consisting mainly of insoluble iron species, accumulate or deposit in the steam generators as sludge. This sludge accumulation results in low-flow, steam blanketed areas where ultra-trace ionic impurities present in the feedwater can concentrate by many orders of magnitude resulting in a highly corrosive local environment. Resulting damage to steam generator components can cause forced outages, tube plugging (loss of output) and ultimately, replacement of steam generators at a cost in the millions of dollars. To put the problem in perspective, the Electric Power Research Institute recommends a maximum sludge pile depth of between 0.42 and 0.85 cm [1]. To achieve these goals, utilities may spend US\$ 8000–10 000 *per kg* to reduce steam generator sludge. The condensate (condensed steam) flows through mixed bed ion exchangers to remove impurities, then is pH adjusted with ammonium hydroxide or morpholine, and hydrazine for removal of oxygen. The condensate becomes feedwater which is heated by a series of heaters before being introduced into the steam generators.

Domestic BWRs and PWRs usually operate continuously for an eighteen month fuel cycle. If the correct chemistry and operational controls are not enforced for this period, corrosion of plant systems, especially feedwater piping, could be significant. These corrosion products must be minimized and removed from steam generators to prevent loss of heat transfer efficiency in PWRs and minimized in BWRs to prevent cladding defects in the fuel. Corrosion transport studies have been conducted by the Electric Power Research Institute [2] to help domestic nuclear plants understand corrosion mech-

anisms and to recommend treatment to minimize corrosion impacts. To date, these studies have measured amounts of the major corrosion products, iron and copper. Limited solubilities of these corrosion products in the feedwater complicates taking a representative sample, requiring concentrating of these impurities from large sample volumes, and a lengthy lab analysis. Methods of many steps tend to introduce error and are not timely for making system corrections on a "real time" basis.

The importance of corrosion control continues to drive the need for a fast, reliable method of corrosion monitoring. In support of this quest, this study evaluates manganese which, as a component of carbon steel [3], can also be accurately determined in the pg/ml level by on-line ion chromatography (IC).

EXPERIMENTAL

Instrumentation

All chromatography in this study was performed using a Dionex (Sunnyvale, CA, USA) series 8100 ion chromatograph. Channel one was set up for transition metal analysis and channel two was set up for the simultaneous determination of monovalent and divalent cation analysis. The ion chromatograph was interfaced with a multichannel data acquisition and control system consisting of a Dionex Autoion 300 computer interface, Hewlett-Packard (Palo Alto, CA, USA) System 300 desk top computer and Hewlett-Packard model 2930 printer. Sample delivery was accomplished using a Dionex sample selection module. Dionex AI 300 software provided data acquisition, data reduction and control of the ion chromatograph.

Corrosion data was collected using NUS (Pittsburgh, PA, USA) corrosion product monitors with Millipore (Bedford, MA, USA) 0.45- μ m particulate filters and Gelman Sciences (Ann Arbor, MI, USA) cation-exchange membrane filters. After acid digestion, the filter solutions were analyzed for iron and manganese using a Perkin-Elmer (Norwalk, CN, USA) Model 5100 atomic absorption spectrophotometer for flame analysis methods. For trace analysis, the Model 5100 was coupled with an HGA-600 Zeeman graphite furnace.

Reagents and standard solutions

The chemicals used in this study were of anal-

ytical-reagent grade unless otherwise noted. Standards were either commercially available atomic absorption standards, or prepared by dissolving the appropriate amounts of salts in deionized water, then stored in polypropylene containers. The water used was plant-produced demineralized water passed through a Barnsted Nanopure (Barnsted/Thermolyne, Dubuque, IA, USA) water system.

The eluent used for cation analysis was a mixture of dilute Ultrex (J. T. Baker, Philipsburg, NJ, USA) hydrochloric acid and 2,3-diaminopropionic acid monohydrochloride (DAP) (Fluka, New York, NY, USA). Tetrabutylammonium hydroxide (TBAOH) (Southwestern Analytical, Austin, TX, USA) was used as the regenerant.

The eluent used for transition metal analysis contained pyridine-2,6-dicarboxylic acid (PDCA), (Kodak, Rochester, NY, USA), glacial acetic acid (J. T. Baker), and sodium acetate (EM Science, Gibbstown, NJ, USA). The post-column reagent contained 4-(2-pyridylazo)resorcinol (PAR) (Fluka, New York, NY, USA), glacial acetic acid and ammonium hydroxide (J. T. Baker).

Columns

All columns used in this study were manufactured by Dionex. The columns used for cation analysis were an IonPac CS10 analytical column, a CG10 guard column, and a trace cation concentrator 2 (TCC-2) column. To reduce eluent impurities when a gradient was employed, a cation trap column was placed on the outlet of the eluent pump prior to the injection valve. The trap column function is to "smear out" eluent impurities by preventing the impurities from building up on the analytical column and eluting as a peak as the gradient program is run.

The columns used for transition metal analysis were an IonPac CS5 analytical column, a CG5 guard column, a CG2 concentrator column followed by a mixing tee and a 1500- μ l beaded reaction coil. The post-column reagent was introduced to the eluent at the mixing tee then allowed to react in the beaded reaction coil and detected on the visible detector at 520 nm.

PROCEDURES

Standards and samples were analyzed for manga-

nese by cation and transition metal IC. The cation channel was operated by employing a gradient program in both the ammonia and morpholine matrix. The conditions were an eluent flow-rate of 1.0 ml/min starting with 20 mM HCl/0.35 mM DAP and after injection a 3-min ramp to 50 mM HCl/14 mM DAP. A cation micromembrane suppressor II (CMMS-II) was used to lower the background conductivity to between 2 and 6 μ S. The regenerant was 100 mM tetrabutylammonium hydroxide with a flow-rate of 10 ml/min. employing a Dionex AutoRegen system. The overall backpressure of the system ranged between 900 and 1200 p.s.i.g.

The transition metal channel consisted of an eluent which contained 6 mM PDCA/50 mM sodium acetate/50 mM acetic acid at a flow-rate of 1.0 ml/min. The post-column reagent was introduced at the mixing tee at a flow-rate of 0.5 ml/min and contained 0.2 mM PAR/3.0 M ammonium hydroxide/1.0 M acetic acid. This mixture was allowed to react in a 1500- μ l beaded reaction coil and the resultant metal complexes were detected on a visible detector at 520 nm.

Corrosion product filters were acid digested and analyzed by atomic absorption spectrophotometry in accordance with Electric Power Research Institute guidelines [4]. The calibration standards were prepared from separate stock μ g/ml standard solutions and placed in the standard preparation module for dilution to calibration levels. The sample preparation module allows for automatic *in situ* preparation of trace (pg/ml) standards to prevent contamination from handling. The precision of the ion chromatography methods was measured continuously by the AI 300 software for up to 202 data points before the file started overwriting. All statistical data were reviewed by use of the trend file function.

In all methods a three-level multicalibration was performed. For the transition metal analysis of manganese 10 ml of standard and sample were concentrated. For the cation analysis of manganese 25 to 50 ml of sample and standard were concentrated except for samples containing up to 7 mg/ml morpholine. In standards and samples containing morpholine only 15 ml could be concentrated before the concentrator began to overload. The corrosion product filters were placed in-line and the average sample volume on each filter was approximately 100 l.

RESULTS AND DISCUSSION

The detection of manganese by ion chromatography has received some attention in the past [5-7]; however, the use of manganese as an indicator of corrosion in power plants is a novel idea. The presence of significant quantities of manganese was first observed in the secondary system of the Surry Power Station. An unknown peak which interfered with magnesium was observed in chromatograms obtained with the Dionex Fast Cation column set. This same peak was also observed at the US-TVA Sequoyah Power Station. Dionex personnel [8] suggested that this unknown peak was probably due to manganese. The identity of the unknown peak was later confirmed by spiking samples with manganese standards.

The on-line ion chromatographs were calibrated for manganese in accordance with the conditions discussed in the experimental section. Initial relative standard deviations (R.S.D.) of standards and samples were unacceptably high (45%). A review of the phase diagram [9] for manganese showed the sample pH was critical in order to ensure that manganese remained in the Mn^{2+} form (see Fig. 1). As a result, all standards and samples were acidified to a pH of *ca.* 4 with Ultrex-grade hydrochloric acid.

The acidification step was performed on line using the Dionex sample preparation module. Acidification reduced the R.S.D. to approximately 20%. The on-line ion chromatographs were operated under these conditions for the rest of the study. Fig. 2 shows an example of the second level calibration of the cation channel using the CS10 column and morpholine matrix. Fig. 3 shows an example of the second-level calibration of the transition metal channel. The linearity of the manganese response at ultra-trace (pg/ml) levels using the CS10 method is demonstrated in Fig. 4.

A significant quantity of manganese was detected in the steam generator blowdown samples during a "hideout return" study conducted at the Surry Power Station Unit 1 in late 1990. The process known as "hideout" results from the concentration of impurities by boiling in flow-restricted regions of PWR steam generators (S/G) such as S/G crevices. Impurities which are concentrated in these regions during power operation will "return" from hideout to the steam generator bulk water during shutdown and subsequent cooldown. Both the cation (CS10) channel and transition metals channel showed concentrations as high as 100 ng/ml. GEBCO Engineering was contracted by the Virginia Electric and Power Company to assist in the evaluation of hideout

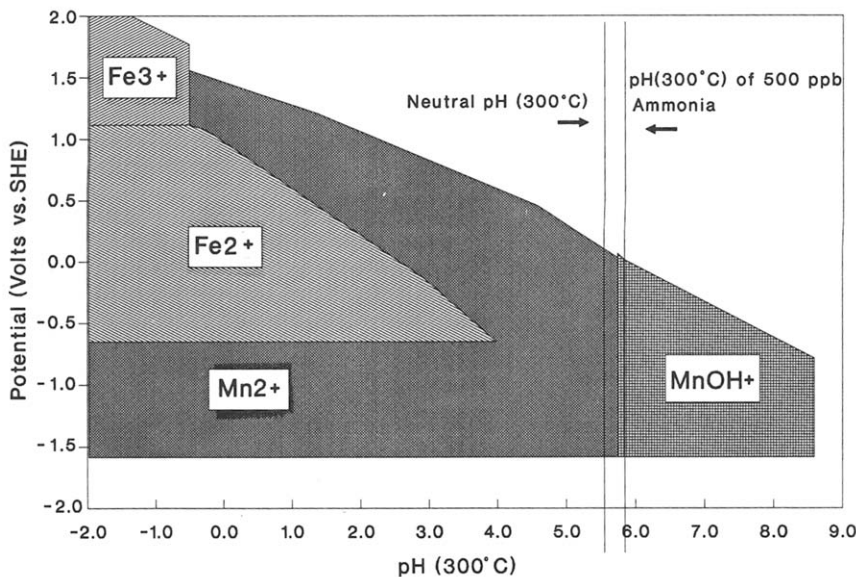


Fig. 1. Partial phase diagrams for iron and manganese at 300°C. SHE = standard hydrogen electrode; ppb represents ng/ml.

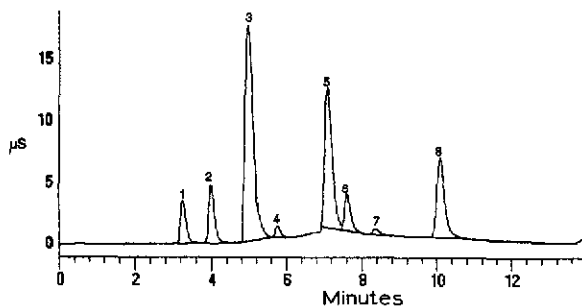


Fig. 2. Autocal 2 in a morpholine-ammonia matrix. Peaks: 1 = lithium (1 ng/ml); 2 = sodium (1 ng/ml); 3 = ammonia (150 ng/ml); 4 = potassium (1 ng/ml); 5 = morpholine (5 µg/ml); 6 = magnesium (2 ng/ml); 7 = manganese (2 ng/ml); 8 = calcium (2 ng/ml).

return data. In their report to Virginia Power, GEBCO suggested that based on their analysis of the data, there was a very strong possibility that the manganese observed during hideout return had originated from corrosion of secondary system piping and components. To attempt to confirm this hypothesis the following test plan was designed to obtain the necessary plant data: (1) conduct mass balance studies to confirm the source of manganese in the secondary system; (2) confirm the identity of manganese in plant samples using alternate analytical methods; (3) perform concurrent monitoring of secondary samples using on-line IC and corrosion product (CP) sampling and analysis by atomic absorption spectrophotometry; (4) attempt to establish a relationship between total iron (using CP

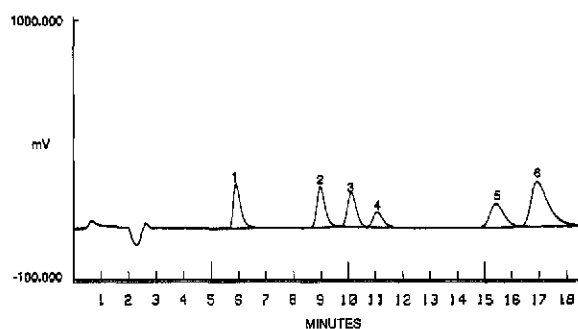


Fig. 3. Autocal 2 transition metals channel. Peaks: 1 = iron(III) (2.5 ng/ml); 2 = copper(II) (2.5 ng/ml); 3 = nickel(II) (2.5 ng/ml); 4 = zinc(II) (2.5 ng/ml); 5 = manganese(II) (5.0 ng/ml); 6 = iron(II) (5.0 ng/ml).

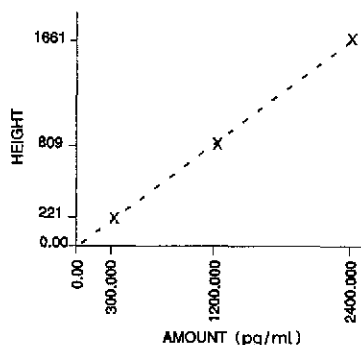


Fig. 4. Manganese low level calibration plot.

analysis) and soluble manganese (using on-line IC) in final plant feedwater.

A mass balance study was conducted at Surry Unit 1 in April, 1991 just three months after unit startup from a refueling outage. The results of this study are shown in Fig. 5. The purpose of the mass balance study was to account for the manganese in the secondary system on a mass transport basis. This approach is used in power plants to identify sources of impurities since many streams are combined to make up the final feedwater. The mass balance identifies the quantitative contribution of each of these streams to the feedwater. From Fig. 5, it was apparent that a significant quantity of the manganese in the final feedwater was contributed by the feedwater piping and components, *i.e.*, the feedwater mass transport rate was nearly double the sum of the polisher effluent and heater drains mass flow-rates. This data strongly indicated that the manganese in the secondary system was originating from corrosion of carbon steel components and therefore should be indicative of total secondary system corrosion.

During the Surry Unit 2 shutdown in the spring of 1991, a second hideout return study was conducted. As in the previous (Unit 1) study, significant concentrations (> 100 ng/ml) of manganese were detected in steam generator blowdown samples analyzed using on-line cation and transition metal IC. To conclusively confirm the presence of manganese, grab samples were collected during the hideout return test period and analyzed using atomic absorption spectrophotometry (AAS). As shown in Fig. 6, the grab sample-AAS results agreed well with the on-line IC data. Figs. 7 and 8 are examples of

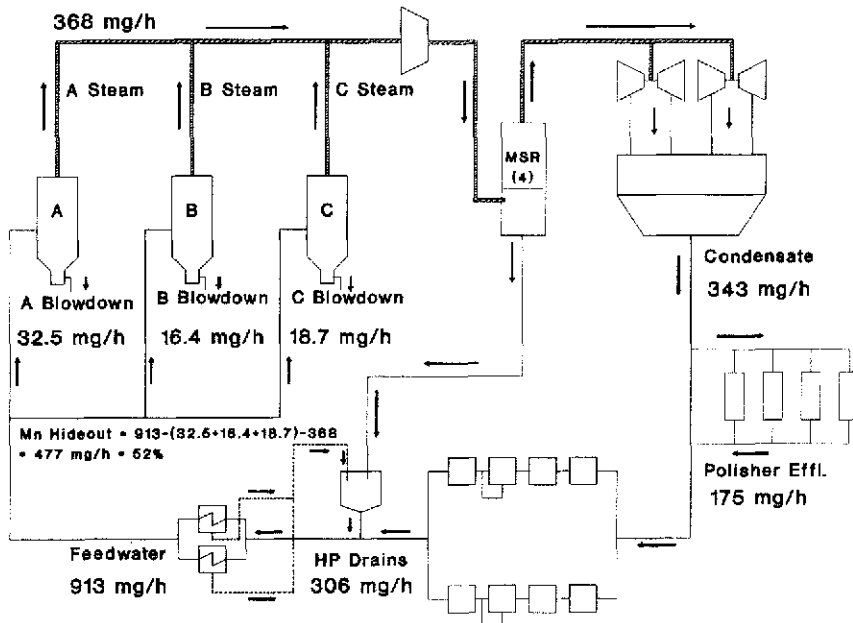


Fig. 5. Surry Unit 1 manganese mass transport from April 21-25, 1991 IC Data.

Unit 2B steam generator blowdown chromatograms of the cation and transition metals channels respectively during this study.

Concurrent monitoring of secondary system samples for manganese by conventional corrosion filter product methods previously described, and on-line IC commenced in April, 1991 and continued through July, 1991. As stated in item 3 above, the

purpose of this portion of the study was to determine the long-term stability of the manganese data and the relationship between soluble manganese (IC) data and corrosion product iron data to determine whether a correlation could be established. Since the IC methods measure only soluble manganese, it was critical to first determine the percentage of soluble *versus* total manganese in plant feedwater samples.

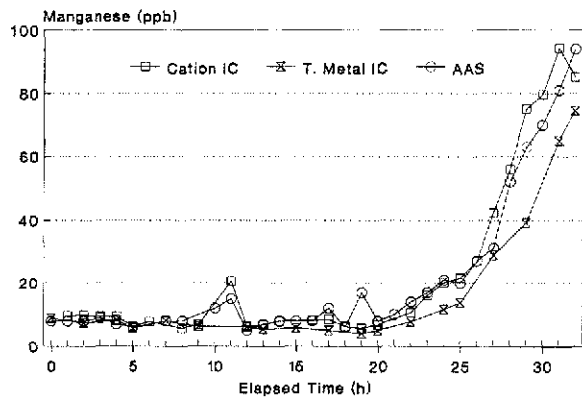


Fig. 6. 2C steam generator manganese hideout return comparison of cation IC, transition (T.) metal IC and atomic absorption spectrophotometry (AAS).

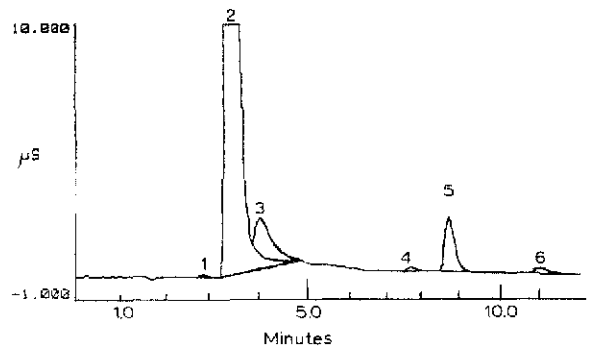


Fig. 7. Surry 2B steam generator cation method. Peaks: 1 = sodium (99.0 pg/ml); 2 = ammonium (125.1 ng/ml); 3 = potassium (139.0 pg/ml); 4 = magnesium (91.0 pg/ml); 5 = manganese (3.21 ng/ml); 6 = calcium (24.9 pg/ml).

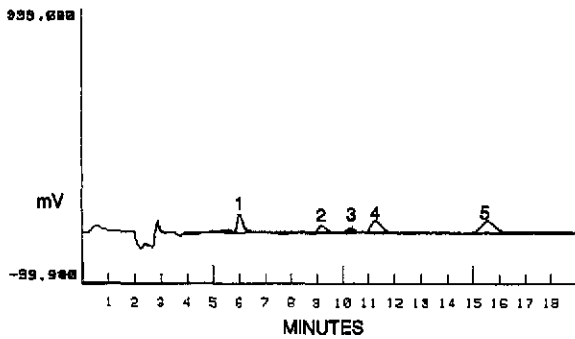


Fig. 8. Surry 2B steam generator transition metals method. Peaks: 1 = iron(III) (1.797 ng/ml); 2 = copper (527.0 pg/ml); 3 = nickel (228.0 pg/ml); 4 = zinc (3.391 ng/ml); 5 = manganese (3.809 ng/ml); 6 = iron(II) (below detection limit).

If the soluble/total manganese ratio was not *ca.* 1.0, or varied significantly, further efforts would not have been warranted. Fig. 9 shows manganese solubility data for the study period from April through July, 1991 as measured by conventional corrosion product filter methods. This data clearly indicated that manganese in the feedwater was >90% soluble in contrast to iron which was <40% soluble.

A second key consideration was the relative agreement between manganese results obtained by on-line IC and corrosion product filter analysis. Fig. 10 shows the results of samples analyzed by both methods during the period from April 22–May 13, 1991. Each IC data point represents the average of all samples analyzed during the 24-h period (typically 2 to 4). Because of the time-consuming nature of the corrosion product method and the necessity to pass very large volumes of sample through the particulate and ion exchange filters to obtain adequate sensitivity, fewer data points were obtained for the corrosion product method. Considering the ultra-trace sample concentrations (200 to 300 pg/ml) in feedwater, agreement between the two methods was quite good however, there was a bias between the two methods. This was not surprising considering the differences is not only the analytical techniques, but also the sampling methods. In addition, the IC method was obviously much better able to detect day-to-day fluctuations on a real-time basis.

As outlined in item 4 above, the final phase of the study was to attempt to determine whether a correlation could be established between the on-line IC manganese data and the corrosion product iron data. In order to establish such a correlation, it was critical that the ratio of soluble manganese to total

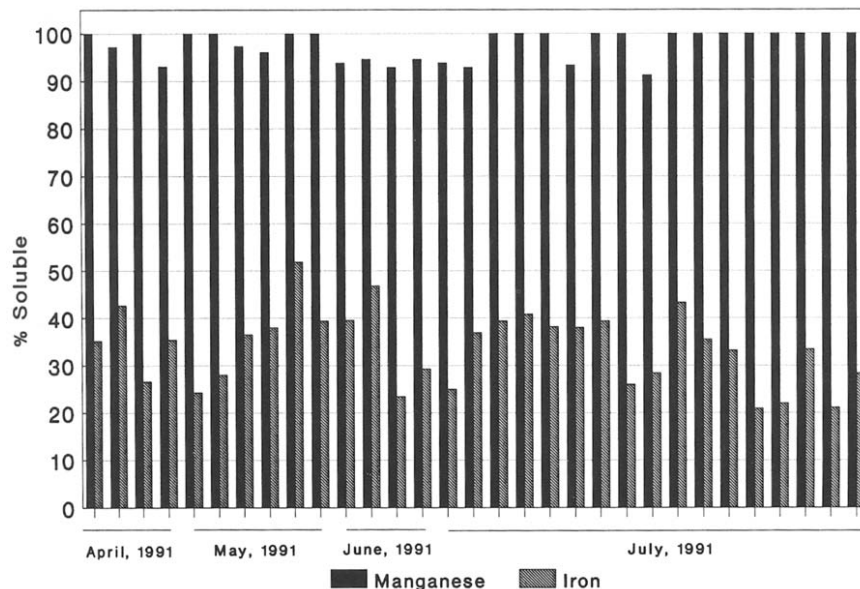


Fig. 9. Surry Unit 1 feedwater manganese and iron solubility April 22–July 30, 1991.

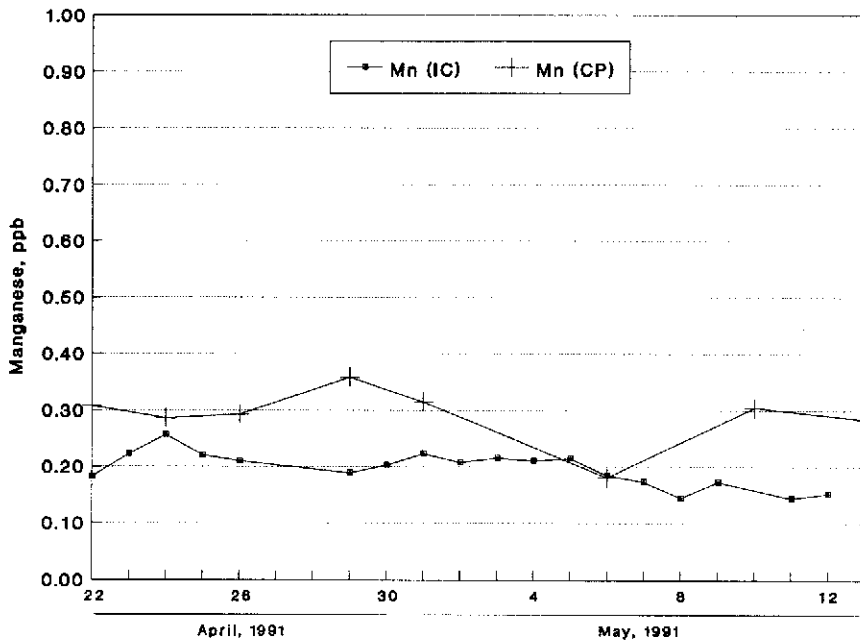


Fig. 10. Surry Unit 1 feedwater manganese: comparison of IC and corrosion product data.

iron remain relatively constant under steady-state plant conditions. The final phase of the study was to use the on-line IC manganese data to predict the total feedwater iron concentration and compare

these predictions to measured values obtained from corrosion product analyses. A correlation constant was established using the total manganese to iron ratio and an offset value to account for the consis-

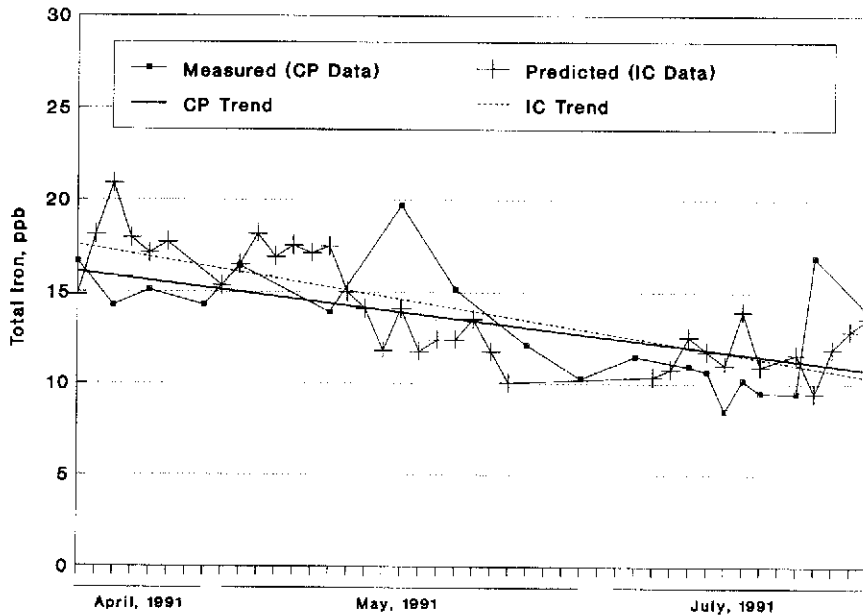


Fig. 11. Surry Unit I feedwater under steady-state conditions.

tent difference in manganese results obtained by on-line IC and the corrosion product method. Total iron was predicted from the IC data by simply multiplying the IC result by the correlation constant. Fig. 11 shows the results of these comparisons for the three-month study period. While there were significant differences between some of the individual predicted and measured values, the overall agreement was excellent. Trend lines for the predicted and measured iron concentrations were nearly identical.

CONCLUSIONS

On the basis of the data presented above, the authors preliminary conclusion was that on-line monitoring of soluble manganese could be used effectively as an indicator of feedwater corrosion product transport in the secondary system of the Surry Station. This is due to the >90% solubility of manganese *versus* the <40% solubility of iron observed during the study. Testing is currently underway at the US-TVA Sequoyah and Browns Ferry Power Stations to determine whether similar correlations can be established for these plants. As stated previously, the use of morpholine for pH control at Sequoyah (*vs.* ammonia at Surry) complicates the chromatography and limits the sample preconcentration volume. At the Browns Ferry Station (BWR) the only additive is oxygen in the feedwater which may influence the solubility of manganese as seen in Fig. 1. Research is underway to attempt to resolve these difficulties and to improve sensitivity and R.S.D.s. It is strongly emphasized that the correlation between soluble manganese and total iron is highly plant-specific since the alloy composition of plant piping and components varies considerably among plants of similar design. The authors are strongly encouraged however, by the results obtained to date. The ability to monitor corrosion of power plant systems on an on-line, real-

time basis would provide power plant chemists with a means of assessing potential damage to critical plant components on a timely basis, and to evaluate the effectiveness of alternate water treatment schemes.

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