

Jo Savelkoul  
Peter Janssen  
Hans Verhoef

## Monitoring of First Condensate Corrosion (FCC) in Industrial Steam Systems

### INTRODUCTION

DSM is a highly integrated international group of companies that is active worldwide in the field of life science products, performance materials, polymers, and industrial chemicals.

DSM's largest production site is at Geleen and the plants located on it are highly integrated. Its total area is about 800 hectares and it accommodates 57 chemical and petrochemical plants, including two ethylene and two ammonia plants. The total production output is over seven million tons of a wide variety of products, a number of which are used as feedstock in downstream plants.

Many processes operate at elevated temperatures and the energy needed or released in them is often exchanged with other processes in the form of steam. Steam generation is decentralized using steam generators and waste-heat boilers operating at pressures of 3 to 140 bar. The design and operation of steam boilers and condensers are determined in part by the type of process, which is why the designs are often unconventional. Besides in the chemical plants, steam is also generated in three combined heat and power plants. The aggregate on-site steam generating capacity amounts to about 2,500 t h<sup>-1</sup>. Distribution systems are available for 3, 12, 18, 26, 42, 79, 95 and 140 bar steam.

Steam treatments are designed to suit particular plant conditions, such as pressure level, construction materials and water quality, and employ common conditioning agents, including ammonia, caustic, trisodium phosphate, hydrazine, morpholine, and polyamine (Helamin). Demineralized river water and treated or untreated plant condensates are used as boiler feed water. The feed water contains humic acids from the demineralized water as well as traces of organic contaminants from condensates. Acidic decomposition products of these impurities are spread throughout the site via the steam distribution systems. Under condensing conditions at temperatures of 50 to 200 °C, these acidic products may initiate FCC, which in turn may lead to serious attack on equipment items such as turbines (Figure 1) and steam condensers (Figure 2).

### CORROSIVITY OF FIRST CONDENSATE AND AVAILABLE MONITORING TECHNIQUES

The steam leaving steam boilers contains organic contaminants and their decomposition products, partly in the form of acids. These acidic contaminants are neutralized as the steam condenses by alkalizing the steam, mostly by adding ammonia and amines to the boiler feedwater. The condensation process is not yet fully understood. Even when the condensing steam contains an excess amount of alkaline substances and has a high pH, localized corrosion, in particular FCC, occurs where the steam first condenses. Such corrosion is clearly indicative of acid conditions. These conditions might be explained by carbon dioxide and organic acids, possibly in the form of more complex and higher boiling compounds, dissolving more rapidly in the first condensate than the ammonia and amines added. Consequently, analysis of condensate samples may not necessarily reveal the exact corrosion mechanism.

As condensation continues, the ammonia and amines present also dissolve, the pH increases, and corrosion eventually ceases. The iron that has meanwhile dissolved because of acid corrosion is then converted into magnetite, which leads to deposits and to fouling of the equipment.



Figure 1: First Condensate Corrosion: Damage to a Turbine.

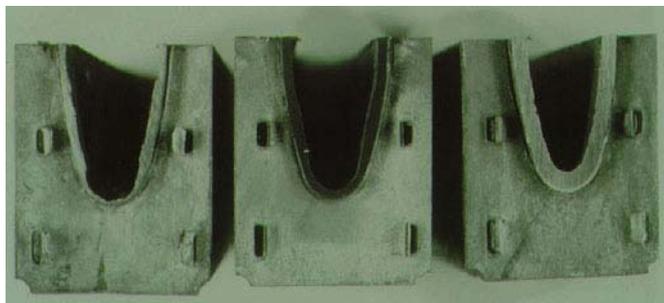


Figure 2: First Condensate Corrosion: Damage to a Steam Condenser.

At the current time, two monitoring systems for measuring the corrosivity of the first condensate are available: the Early Condensate Sampler [1-6] and experimental turbines (7-15).

In the Early Condensate Sampler, contaminants are removed from the steam in relation to the amount of condensate produced from the steam. The concentrations of the various components are determined by chemical analysis and high-performance liquid chromatography. The pH, and so the corrosivity, of the first condensate is calculated from these analyses. The advantage is that the equipment can be connected to any steam system. However, a restriction is that it is not really the very first liquid phase that is collected.

In an experimental turbine, the first condensate formed locally on the turbine blades is discharged through channels

in the turbine blades and is then analyzed. A disadvantage is that these tests can only be carried out with special experimental turbines. It is nearly impossible to translate results to industrial conditions.

In either method, the composition and by derivation the corrosivity of the very first liquid phase is determined through chemical analysis of the acidic and alkaline compounds present in a collected steam condensate sample. Corrosion is assumed to be initiated by the simple compounds identified in the analysis of this condensate sample.

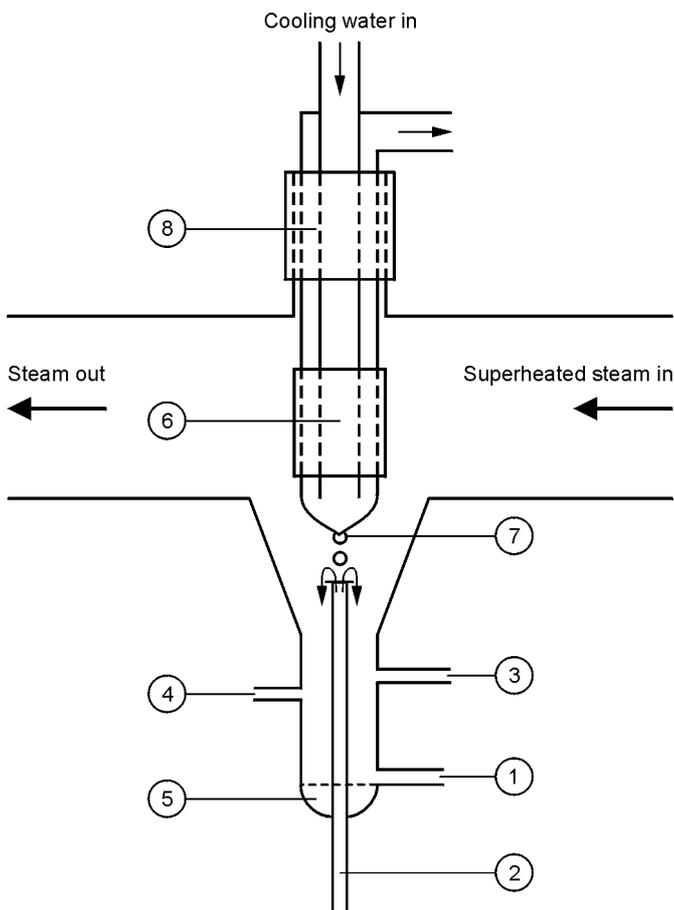


Figure 3: DSM First Condensate Corrosion Probe (FCCP).

- 1 To iron measurement equipment
- 2 Supply of sulfuric acid
- 3 Nitrogen purge
- 4 Maximum level safety overflow suction pump
- 5 First condensate with acid
- 6 First condensate corrosion probe
- 7 First condensate droplets
- 8 Cooler

**DEVELOPMENT OF THE DSM FIRST CONDENSATE CORROSION MONITORING SYSTEM**

As mentioned earlier, the condensation process is by no means fully understood. Moreover, it is almost impossible to analyze the very first liquid phase as it develops. DSM has developed a First Condensate Corrosion Probe (FCCP) [17] for early detection of FCC in spite of these unknowns to optimize the steam conditioning methods.

The system operates on the principle that the very first liquid phase that develops on a cooled carbon steel corrosion coupon causes attack of the steel to a degree depending on the corrosivity of this very first liquid phase and so dissolves more or less iron. As the condensation process continues, the liquid phase grows to form a drop of condensate with a varying chemical composition, but the iron dissolved in the first liquid phase remains in solution.

In the measuring cell (Figure 3) steam, which at this point is slightly superheated, condenses on the cooled FCCP. The condensate is carried away along the coupon as quickly as possible and is then subjected to Fe analysis. The extent of attack or, in other words, the relative corrosion rate, is determined on the basis of this analysis. Higher corrosion inhibition leads to a lower Fe concentration, and the converse is also true.

The condensate that forms on the FCCP is immediately collected in diluted sulfuric acid to keep the iron dissolved. The iron content of this acidic solution, being a measure of the steam's corrosivity, is continuously measured. The area around the funnel is inerted by a small nitrogen stream to prevent alkalinizing agents from being dissolved.

The FCCP was developed and tested in a laboratory set-up (Figure 4). A distinct relationship was established between the measured amount of iron in the first condensate and the pH of the final condensate (see also Figure 6).

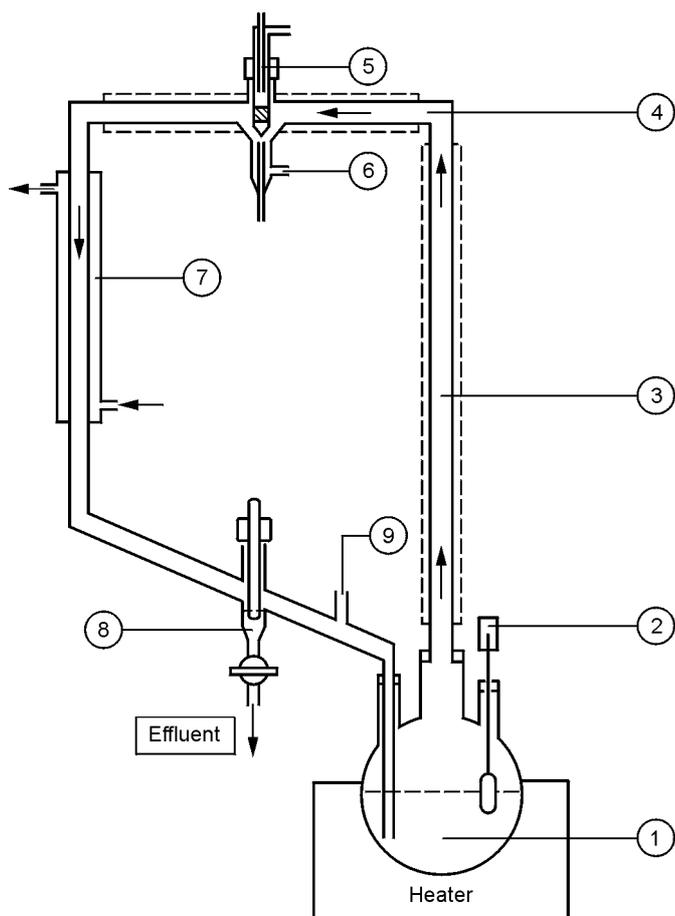


Figure 4: Laboratory Set-Up with DSM First Condensate Corrosion Probe (FCCP).

Commentary to Figure 4:

- 1 Solution in a glass bottle
- 2 Level indicator with a blowdown pump
- 3 Steam superheating
- 4 Steam flow
- 5 First condensate corrosion probe
- 6 First condensate reservoir
- 7 Condenser
- 8 pH measurement of the effluent
- 9 Nitrogen purge for inert shielding

## SYSTEM FOR FIELD MONITORING

A monitoring system including the FCCP (Figure 5) was mounted on a trailer for measurements in the field. An identical system, without FCCP, was installed in parallel. In the latter system, the first condensate is collected as such (without acid) for determining the pH and chemical composition through chemical analysis. The analysis can provide a clue as to the possible cause of corrosion and allows the effects of countermeasures, for instance in boiler feedwater preparation, to be assessed.

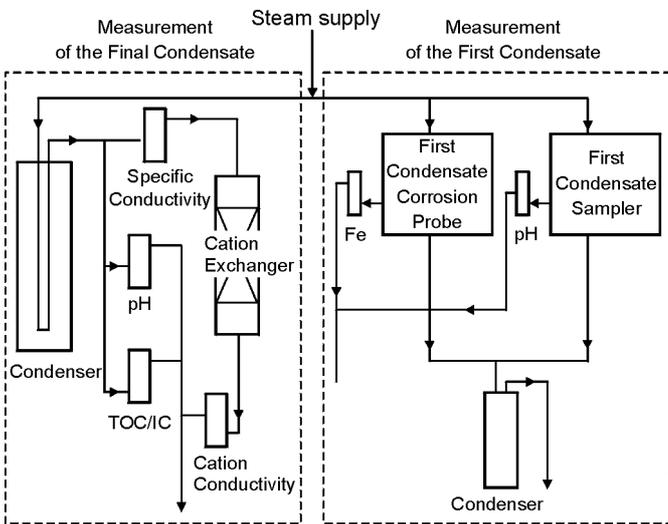


Figure 5: Schematic Diagram of Field Monitoring System with FCCP.

It is also able to measure customary condensate quality parameters including pH, TOC, TC, total conductivity and conductivity after cation exchanger (cation conductivity). Data management is fully computerized.

While a measurement is in progress, the effects of varying the steam-conditioning program can be assessed without delay. Thus, steam conditioning can be optimized on-line. The system can be wired up at almost any location at the site.

## CASE STUDIES

### Case 1

A carbon steel air heater connected to the 26 bar steam system often developed FCC (Figure 1). The steam was alkalinized with ammonia to pH 9.3-9.8. Cation conductivity was in the 0.5-0.7  $\mu\text{S cm}^{-1}$  range. Investigation with the aid of the FCCP revealed that the steam became less corrosive when we increased the pH of the final condensate to 10.3 (Figure 6).

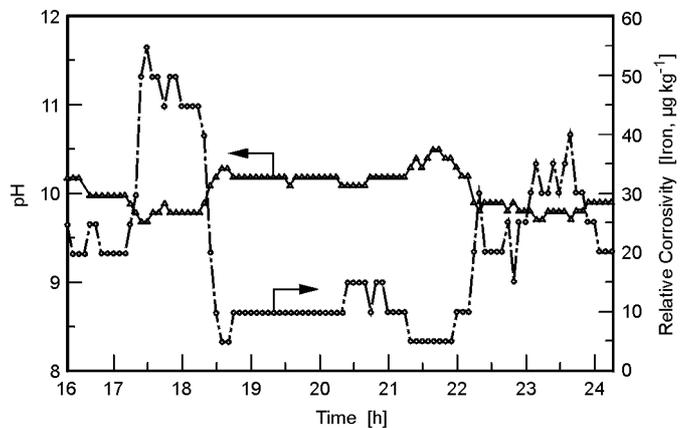


Figure 6: Relative Corrosivity ( $\mu\text{g kg}^{-1}$  Fe) of the Steam as a Function of the pH of the Final Condensate.

On all occasions, the pH of the first condensate in the parallel monitoring system was 1 to 1.5 pH units lower than the pH of the final condensate (Figure 7).

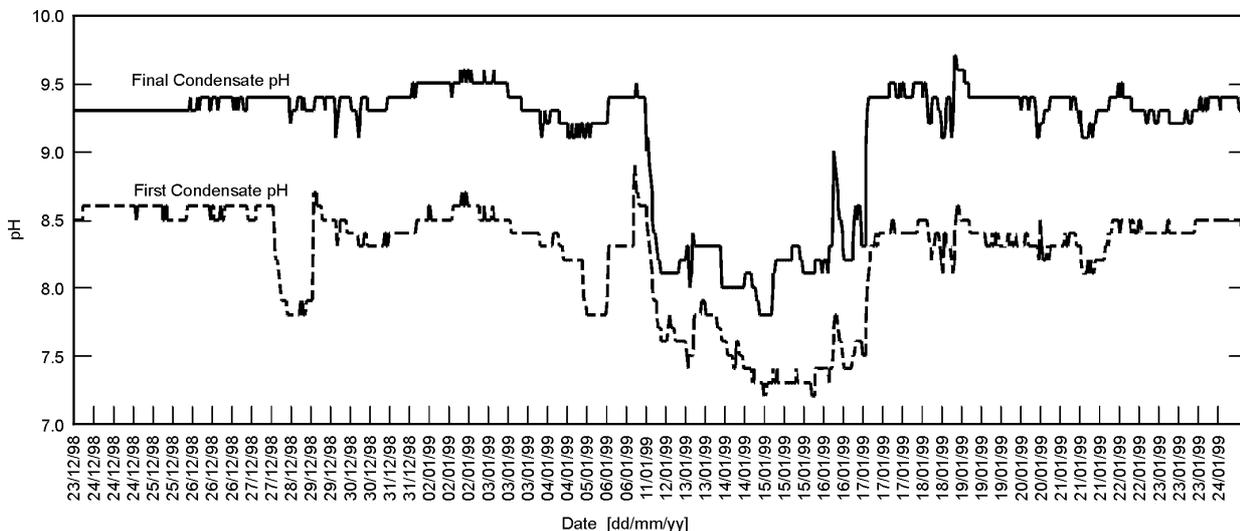


Figure 7: pH of the First Condensate Relative to the pH of the Final Condensate.

**Case 2**

At some point in the past, carbon steel equipment items in which 18 bar steam condenses exhibited FCC. The boiler feedwater in the steam supply system was alkalinized with ammonia and morpholine to pH 9.5 to 10. Nevertheless, corrosion continued to occur at temperatures of about 200 °C. Acidic impurities in the steam proved to consist of decomposition products of morpholine. On suspending the addition of morpholine, the cation conductivity of the steam decreased dramatically (Figure 8).

Steam in the 18 bar distribution system is discharged by a steam turbine operating at 125 bar and 540 °C. Morpholine is added in order to prevent corrosion of the boiler. FCC measurements indicated that fluctuations in the addition of morpholine result in corrosive conditions (Figure 9).

**Case 3**

The turbine in an 80 bar steam system carrying superheated turbine steam of 480 °C was fouled by phosphates and silicates when the steam drum was overloaded. The boiler

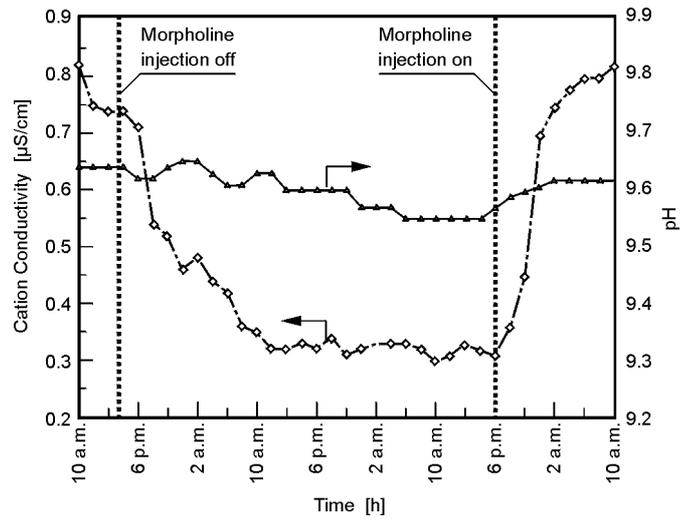


Figure 8: Cation Conductivity and pH of Steam with and without Addition of Morpholine.

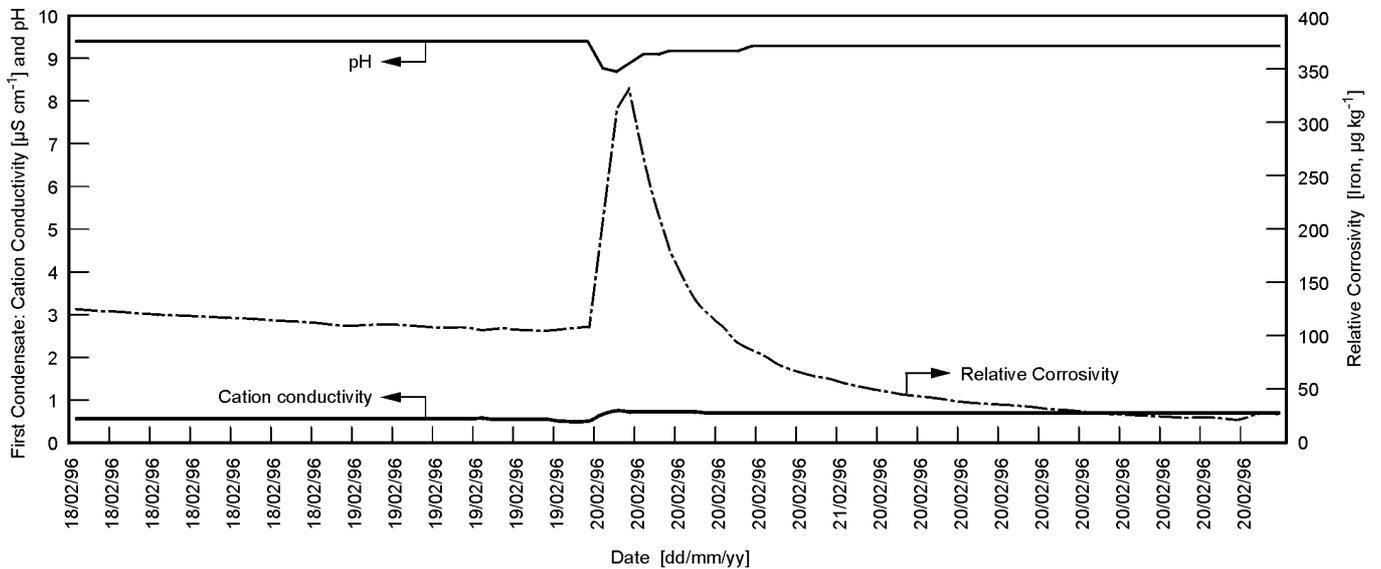


Figure 9: Corrosion Monitoring: 18 bar Steam, System #N4.

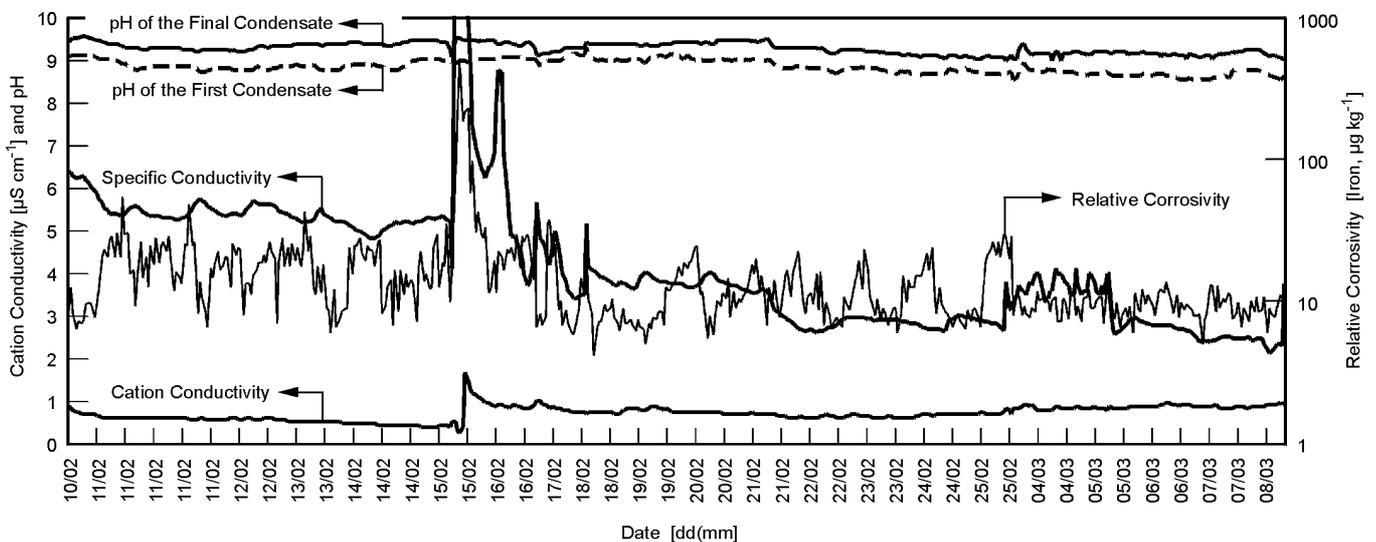


Figure 10: Corrosion Monitoring: 12 bar Steam, System #S5.

feedwater used for this steam system is about 75% fresh demineralized river water that still contains humic acids. Consequently, the cation conductivity of the steam is always 0.5-1.5  $\mu\text{S cm}^{-1}$ . The traditional conditioning technique with ammonia and trisodium phosphate was replaced with one involving Helamin, a polyamine. With the aid of the FCCP, we established to what extent in how far the steam corrosivity and steam alkalization were under control.

The polyamine addition had no significant effect on the cation conductivity of the steam.

It was remarkable that the difference in pH between the first condensate and the final condensate under the given measuring conditions was only about 0.5 pH units (Figure 10). In the systems that are not treated with polyamine, this difference is usually greater than one pH unit.

Since operating with polyamine conditioning for five years, no corrosion problems have occurred in this steam system.

## CONCLUSIONS

The DSM First Condensate Corrosion Probe is well able to monitor steam corrosivity in the field and facilitates optimizing steam conditioning systems. Under certain conditions, adding morpholine appears to promote rather than prevent corrosion.

Treatments that employ polyamines have proved a suitable alternative to conditioning with ammonia and trisodium phosphate for both boiler water and steam.

## REFERENCES

- [1] Bodmer, M., Svoboda, R., *Method and Apparatus for Detecting Corrosion in Steam Turbine Installations*. United States Patent 4,283,200.
- [2] Svoboda, R., Sandmann, H., Romanelli, S., Bodmer, M., *Proc., 5th International Conference on Water Chemistry of Nuclear Reactor Systems, 1989*. British Nuclear Energy Society, London, UK.
- [3] Svoboda, R., Sandmann, H., Romanelli, S., Bodmer, M., *Interaction of Iron-based Materials with Water and Steam (Ed. Dooley, B. and Bursik, A.), 1993*. Electric Power Research Institute, Palo Alto, CA, EPRI TR-102101, 32-1 - 32-16.
- [4] Svoboda, R., Sandmann, H., Romanelli, S., Bodmer, M., *Physical Chemistry of Aqueous Systems, Proc., 12th International Conference on the Properties of Water and Steam 1994 (Ed. White, Jr., H.J., Sengers, J.V., Neumann, D.B., and Bellows, J.C.), 1995*. Begell House, New York, N.Y., 720-729.
- [5] Stodola, J. and Svoboda, R., *International Conference, Steam Chemistry - Interaction of Chemical Species with Water, Steam, and Materials during Evaporation, Superheating, and Condensation, 1999*. Paper No. 8.
- [6] Svoboda, R., Bodmer, M., Sandman, H., *PowerPlant Chemistry Seminar "Feedwater and Boiler Water Treatment in Industrial, Co-Generation, and Refuse Incineration Plant and in Units with Heat Recovery Steam Generators", 2000*. PowerPlant Chemistry GmbH, Neulussheim, Germany.
- [7] Vasilenko, G.V., Sutotsky, G.P., *Interaction of Iron-based Materials with Water and Steam (Ed. Dooley, B. and Bursik, A.), 1993*. Electric Power Research Institute, Palo Alto, CA, EPRI TR-102101, 35-1 - 35-19.
- [8] Petrova, T.I., Povarov, O.A., Rigenkov, V.A., Petrov, A.Yu., Rossikhin, L.Ya., Polevoi, E.N., *Vestnik MEI 1995*, No. 3, 61.
- [9] Dooley, R.B., Feldberg, L.A., Kashinsky, V.I., Martynova, O.I., Petrov, A.Yu., Petrova, T.I., Popov S.A., Povarov, O.A., Semenov, V.N., and Troitsky, A.N., *Turbine Steam, Chemistry and Corrosion: Experimental Turbine Tests, 1997*. Electric Power Research Institute, Palo Alto, CA, EPRI TR-108185.
- [10] Petrova, T.I., Povarov, O.A., Semenov, V.N., Kashinsky, V.I., and Petrov, A Yu., *PowerPlant Chemistry 2000*, 2(5), 280.
- [11] Povarov, O.A., Semenov, V.N., Troitsky, A.N., and Dooley, B., *PowerPlant Chemistry 2000*, 2(4), 204.
- [12] Povarov, O.A., Petrova, T.I., Semenov, V.N., Kashinsky, V.I., Troitsky, A.N., Petrov, A.Yu., and Dooley, R.B., *6th International Conference on Cycle Chemistry 2000*, Columbus, OH.
- [13] Dooley, R.B. and Hubbard, D.E., *PowerPlant Chemistry 2000*, 2(7), 389.
- [14] Dooley, B. and McNaughton, W.P., *PowerPlant Chemistry 2000*, 2(12), 709.
- [15] Petrova, T.I., Petrov, A Yu., Zhgenti, J.V., and Dooley, B., *PowerPlant Chemistry 2001*, 3(3), 143.
- [16] Savelkoul, J., Janssen, P., *Watersymposium '99, 1999*. Technology Centre Corrosion, Bilthoven, The Netherlands.