

Operational Experience with Organics in Industrial Steam Generation

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ABSTRACT

In the chemical process industry, the steam cycle is of secondary importance: the (petro)chemical process comes first. High heat flux designs and – generally unavoidable – water quality problems make industrial boilers susceptible to corrosion.

The selected steam cycle treatment has to be tolerant towards (in)organic contaminants. Conventional programs are not always suitable to meet the specific challenges of individual plant steam cycles. Moreover, degradation products of classic organic alkalizing agents like morpholine may worsen the situation in some respect.

A polyamine program can be a worthwhile alternative. Our experience with polyamines so far has been very positive and has made us confident enough to now consider these products for 12.5 MPa steam systems.

INTRODUCTION

The design and operation of waste heat boilers (WHBs) and heat recovery steam generators (HRSGs) in the chemical process industry significantly differs from utility sector practice. In this paper, the differences are highlighted and discussed with particular reference to the authors' operational experience with organic impurities and organic alkalizing agents in the steam systems of DSM and SABIC plants in the Netherlands, particularly in Geleen.

CHARACTERISTICS OF INDUSTRIAL STEAM SYSTEMS

Contrary to in power plants, the design and operating regimes of WHBs/HRSGs in the chemical process industry are dictated by the (petro)chemical process conditions [1]. Steam generation is not the primary purpose of a chemical plant. For instance, an industrial steam generator may have to satisfy the requirement of rapid process fluid cooling in order to arrest unwanted polymerization reactions. Such a requirement often translates to a compact boiler design with locally high heat fluxes, i.e., $800 \text{ kW} \cdot \text{m}^{-2}$ and

up. Especially in vertical designs, the highest heat flux area in the steam generator may coincide with a physical low-point where magnetite can accumulate. The combination of high heat fluxes and fouling makes boilers very sensitive to corrosion damage.

Industrial steam cycles are also characterized by high makeup demands because of water losses to the process due to live steam injection. Furthermore, steam is not only condensed in turbines but also at temperatures of up to $200 \text{ }^\circ\text{C}$ in all kinds of process equipment.

In order to save on water consumption, (potentially) contaminated condensates are typically reused. At the Geleen site (named Chemelot), only the larger plants have their own condensate polishing unit (CPU). Since Chemelot is a large and highly integrated site, smaller plants route their condensates to a central CPU at a demineralized water plant. Because of the risk of cross-contamination of condensates, this approach requires alkalizing programs with a high tolerance towards impurities.

Finally, the industrial steam cycle is generally not monitored as closely as in the utility sector. The (petro)chemical process comes first.

Corrosion damage to boiler tubes in Geleen and elsewhere has made it very clear that fouling of high heat flux zones in boilers must be avoided [2,3]. Given the water quality issues in the chemical process industry described in this paper, there is a need for conditioning chemicals capable of minimizing corrosion product transport in the industrial steam cycle whether by flow-accelerated corrosion (FAC, pre-boiler system), the formation of porous magnetite layers, or first condensate corrosion (FCC, condensate system).

In our experience, the corrosion product transport and deposition problem cannot always be integrally solved using traditional alkalizing programs. Modern treatment programs based on polyamines can be an effective alternative. It is important, however, to understand the deportment and effects of organics throughout the steam cycle.

CORROSION EXPERIENCE WITH ORGANICS IN INDUSTRIAL STEAM SYSTEMS

There are 3 sources of organics in steam systems in the chemical process industry:

1. Makeup water
2. Process contamination
3. Water cycle treatment chemicals

Makeup Water

In the chemical process industry, live steam injection results in water losses from the steam cycle. In extreme cases, no condensate at all is recovered for reuse as boiler feedwater.

In Geleen, demineralized makeup water is prepared from river water containing humic acids and chloride- and sulfate-bearing non-ionic organics. These compounds are only partially or not at all removed by flocculation, filtration and ion exchange. Moreover, leachables from cation exchange resins, in particular sulfonates, also contaminate the demineralized water. Prior to the coming on-stream of a new water plant using membrane technology, demineralized water at the Chemelot site typically contained 400–500 $\mu\text{g} \cdot \text{kg}^{-1}$ total organic carbon (TOC).

In heated feedwater, and, most certainly, in boiler water, the organic impurities introduced to the steam cycle with the demineralized water are (partly) thermally decomposed. The resulting organic and inorganic acids decrease the alkalinity of the feedwater and, depending on such factors as boiler water buffer capacity and acid volatility, the pH of the boiler water.

Figure 1 shows the conductivity of demineralized water from an older water plant at the Geleen site before and after thermal decomposition of organics. In this case, thermal decomposition was carried out in a continuous laboratory autoclave.

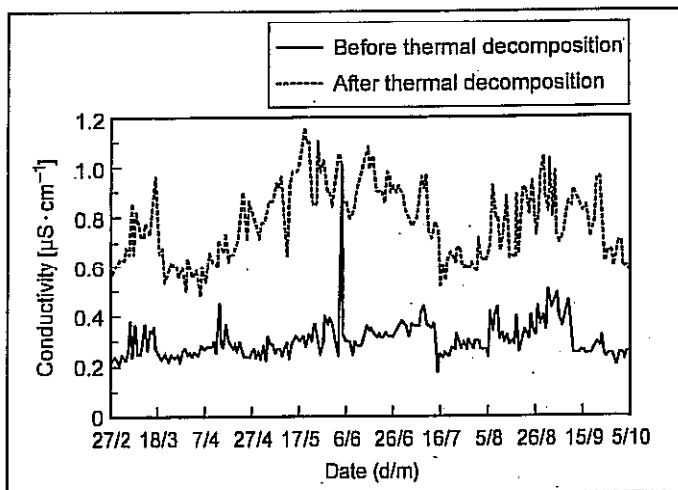


Figure 1: Conductivity of demineralized water before and after thermal decomposition of organics [1].

In order to combat FCC, Chemelot guidelines for steam generation from demineralized water recommend a higher ammonia concentration in steam in the case of condensate with elevated acid conductivity. Table 1 shows the acid conductivity-pH relationships.

In Table 2, the type and concentration range of acids measured in samples of boiler water from an 8.0 MPa boiler in the steam cycle of a nitric acid plant with about 30 % demineralized makeup water are depicted.

Acid conductivity [$\mu\text{S} \cdot \text{cm}^{-1}$]	Recommended pH (at 25 °C)
< 0.2	9.0–9.2
0.2–0.4	9.2–9.5
0.4–0.6	9.5 (copper) – 10
> 0.6	10

Table 1: Internal guidelines for the alkalization of steam with ammonia in case of elevated condensate acid conductivity.

Type of acid	Concentration range [$\mu\text{g} \cdot \text{kg}^{-1}$]
Formic	20–30
Acetic	300–800
Propionic	0–100
Lactic	500–550
Hydrochloric	20–200
Sulfuric	300–500
Nitric	0–5

Table 2: Composition ranges of 8.0 MPa boiler water samples.

Our experiences with the steam system of this nitric acid plant will be discussed in more detail later on. Given the elevated acid concentrations of Table 2, a phosphate program was the obvious boiler water treatment choice. Acids that were not "captured" by the alkaline phosphate contributed to the acid conductivity of the steam condensate and – together with a CO_2 "background concentration" of approximately 200 $\mu\text{g} \cdot \text{kg}^{-1}$ – further increased the risk of FCC. Table 3 shows the type and concentration range of acids measured in samples of turbine condensate in the same period.

Type of acid	Concentration range [$\mu\text{g} \cdot \text{kg}^{-1}$]
Formic	0–15
Acetic	0–50
Propionic	0
Lactic	0–5
Hydrochloric	2–5
Sulfuric	0–10
Nitric	0

Table 3: Composition ranges of turbine condensate samples.

The condensate acid conductivity in this plant averaged 0.3–0.8 $\mu\text{S} \cdot \text{cm}^{-1}$. Although FAC and FCC have given problems, no turbine blade damage has been observed.

Process Contamination

An illustrative example of steam cycle contamination by process impurities can be found in ammonia plants, where, depending on catalyst activity, more or fewer alcohols (methanol) may be formed as unwanted by-products of ammonia synthesis [3]. These alcohols enter the steam cycle via process condensates, which, together with turbine condensate and demineralized water, constitute the feedwater. Since the alcohols are non-ionic, they are obviously not removed in a CPU.

Table 4 shows TOC concentrations (in $\text{mg} \cdot \text{kg}^{-1}$) in feedwater in three different steam generators in ammonia plants at the Geleen site.

In Table 5, the type and concentration range of acids as well as the TOC level measured in samples of Boiler #3 turbine condensate are summarized.

Over the years, the condensate acid conductivity in the ammonia plants has varied from 0.5 to 1.5 $\mu\text{S} \cdot \text{cm}^{-1}$. Despite the occurrence of FAC and FCC no turbine blade damage has been experienced.

Boiler	Operating pressure [MPa]	TOC [$\text{mg} \cdot \text{kg}^{-1}$]
#1	4.0	3
#2	6.8	1
#3	12.5	15

Table 4: TOC concentration in feedwater of three boilers.

Type of acid	Concentration range [$\mu\text{g} \cdot \text{kg}^{-1}$]
Formic	0–20
Acetic	10–70
Lactic	0–30
Carbonic (as CO_2)	50–500

Component	Concentration range [$\text{mg} \cdot \text{kg}^{-1}$]
TOC (methanol)	13–18

Table 5: Composition ranges of turbine condensate samples.

Organic Acids and Boiler Water pH As mentioned before, organic impurities are (partly) degraded or oxidized to short-chain fatty acids and mineral acids upon heating. Certainly in the concentration ranges under consideration

in this section, these may enhance FAC in the pre-boiler system and FCC in the condensate system, and cause an alkalinity loss in boiler water.

Organic acids obscure the true boiler water pH. Given the decreasing strength of common weak organic acids (and organic alkalis) with temperature, it is crucial to understand the difference between the pH at room temperature, pH (25 °C), and the actual pH at the operating temperature of the boiler, pH_T . At the Geleen site, the boiler water pH is controlled so as to satisfy the following requirement of the internal guidelines:

$$\text{pH}_T \geq \text{neutral pH}_T + 1 \quad (1)$$

Organic Water Cycle Treatment Chemicals

All-volatile treatment (AVT) was introduced to overcome the corrosion problems associated with phosphate in high-pressure boilers. AVT programs use amines to control the pH of feedwater, boiler water and steam condensate, the simplest and most widely used amine being ammonia. Blends of amines with different volatilities are common.

With this type of alkalization, it is even more important to bear in mind that pH measurements carried out at room temperature are not representative of pH_T [1]. Furthermore, the pH in a porous magnetite layer cannot be buffered with volatile amines. This is why AVT programs require high-purity boiler water.

Morpholine Case. The 12.5 MPa steam system of one of the naphtha crackers in Geleen has been treated with ammonia-morpholine ever since it came on-stream in the late 70s. The steam cycle features multiple high heat flux HRSGs and two condensation turbines.

Three years after startup of the cracker several HRSGs suffered severe corrosion damage. It was determined that the damage was caused by corrosion of thermally highly loaded heat transfer surfaces fouled with corrosion products resulting from (i) FAC in the pre-boiler system, and (ii) FCC in the large carbon steel air cooled condensers. In order to mitigate corrosion product transport caused by FAC, the operating mode of the pre-boiler system was changed from AVT to high-AVT by increasing the ammonia concentration in feedwater from 0.1–0.2 $\text{mg} \cdot \text{kg}^{-1}$ to 1 $\text{mg} \cdot \text{kg}^{-1}$. This of course gave a 5- to 10-fold increase in the cation load of the condensate polisher. To minimize iron deposition due to FCC, cotton candle filters were also installed in the turbine condensate return lines, since turbine condensate is routed back to the deaerator without treatment in the CPU.

After several years of operation, FCC related problems of end-users of 1.8 MPa export steam of the cracker came to light. Using an in-house developed on-line FCC monitoring technique [4] it was demonstrated that acidic breakdown

Parameter	Unit	FW	BW	Steam/Condensate
pH (25 °C)		9.0–9.5	9.5–10	9.0–9.5
Total conductivity	$\mu\text{S} \cdot \text{cm}^{-1}$	< 15	< 250	< 15
Residual oxygen	$\mu\text{g} \cdot \text{kg}^{-1}$	< 20	–	–
Polyamine	$\text{mg} \cdot \text{kg}^{-1}$	0.5–1	2	0.5–1

Table 6: Site-specific water quality guidelines. FW feedwater BW boiler water

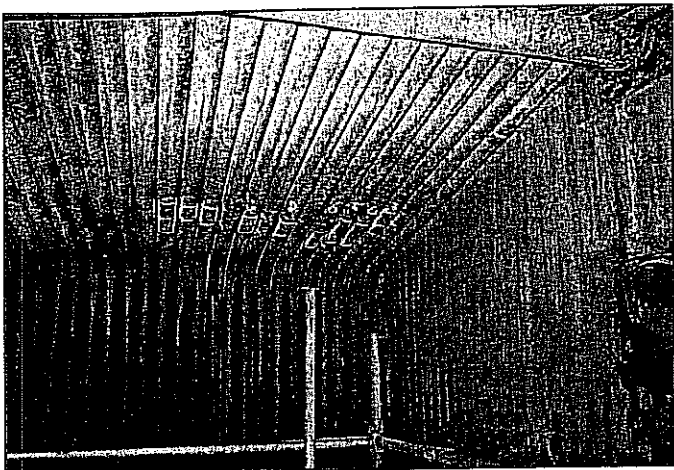


Figure 5: Interior view of an industrial waterwall boiler with marked bulged tubes.

Over a period of 15 years, the problems could not be solved using different conventional treatment programs whether or not supplemented with iron dispersants. With better monitoring equipment in place upsets could be detected but not prevented. Metallic candle filters (temperature!) were installed but by-passed only after a couple of years due to unacceptable pressure drops.

In 1996, a polyamine-polyacrylate treatment using the product Helamin® 906DEA was started. Table 6 shows the current guidelines for safe operation of the steam system. Silica is not an issue on this particular site. Contaminated condensates are routed to the sewer in case of conductivity increases to $> 25 \mu\text{S} \cdot \text{cm}^{-1}$ (!).

No boiler tube failures have occurred and no other damage has been observed ever since, despite major pH excursions. This is significant considering the presence of residual fouling and scaling even after 9 years of operation.

The most troublesome upset was due to the ingress of caustic soda. It took several days to restore the normal boiler water parameters down from pH (25 °C) > 13 with out-of-range conductivities of up to $37\,800 \mu\text{S} \cdot \text{cm}^{-1}$. Whereas the free NaOH concentration corresponding to a conductivity of $37\,800 \mu\text{S} \cdot \text{cm}^{-1}$ amounts to no less than $7 \text{g} \cdot \text{L}^{-1}$, it should be realized that the caustic level in porous magnetite deposits under evaporative conditions may actually have been much higher locally!

During another more recent upset benzoic acid leaked into condensate, ultimately giving boiler water with a pH (25 °C) < 4 (bulk water value). With polyamines, the alkalinity in the film on the tube wall is expected to have been higher, thus providing adequate protection during the incident.

8.0 MPa Steam System

In the mid-90s there were also problems with the 8.0 MPa steam system of a nitric acid plant. As will become clear, the reason for choosing a polyamine treatment program here is completely different from the above case.

There are two nitric acid plants at the Geleen site. Nitric acid is produced by oxidizing ammonia with air at high temperature. The resulting hot nitrous gases are cooled down in a Lamont type, forced circulation boiler.

The boiler in this case was constructed in 1989 and has since continuously been operated to produce 8.0 MPa steam. Saturated steam of 295 °C is superheated to 480 °C and fed to a turbine. Untreated turbine condensate, together with $\approx 30\%$ demineralized makeup, constitutes the feedwater.

Originally, the steam system was alkalinized using ammonia ($0.2 \text{mg} \cdot \text{L}^{-1}$) and phosphate ($2\text{--}6 \text{mg} \cdot \text{L}^{-1}$) due to high levels of TOC in the demineralized makeup water (see section on organics in makeup water). Indeed, over $3\,000 \mu\text{g} \cdot \text{L}^{-1}$ of acids in boiler water have been measured during the phosphate treatment. Hydrazine dosing ($0.05 \text{mg} \cdot \text{L}^{-1}$) was stopped in 1995.

Water/steam separation in the drum was proven to be poor via sodium measurements, particularly after plant capacity upgrades over the years. This led to serious fouling of the low-pressure section of the turbine with sodium phosphate/silicate deposits. At one point, the turbine had to be water flushed once every three months to bring up the steam swallowing capacity to an acceptable level.

When the steam cycle treatment program was reevaluated, it was considered too risky to change over to a classic AVT treatment using ammonia and/or morpholine because of potentially elevated concentrations of chloride- and sulfate-bearing organics in the demineralized makeup water. In 1996, a polyamine program using the product Helamin® 90HTurb was started instead to replace both ammonia and phosphate.

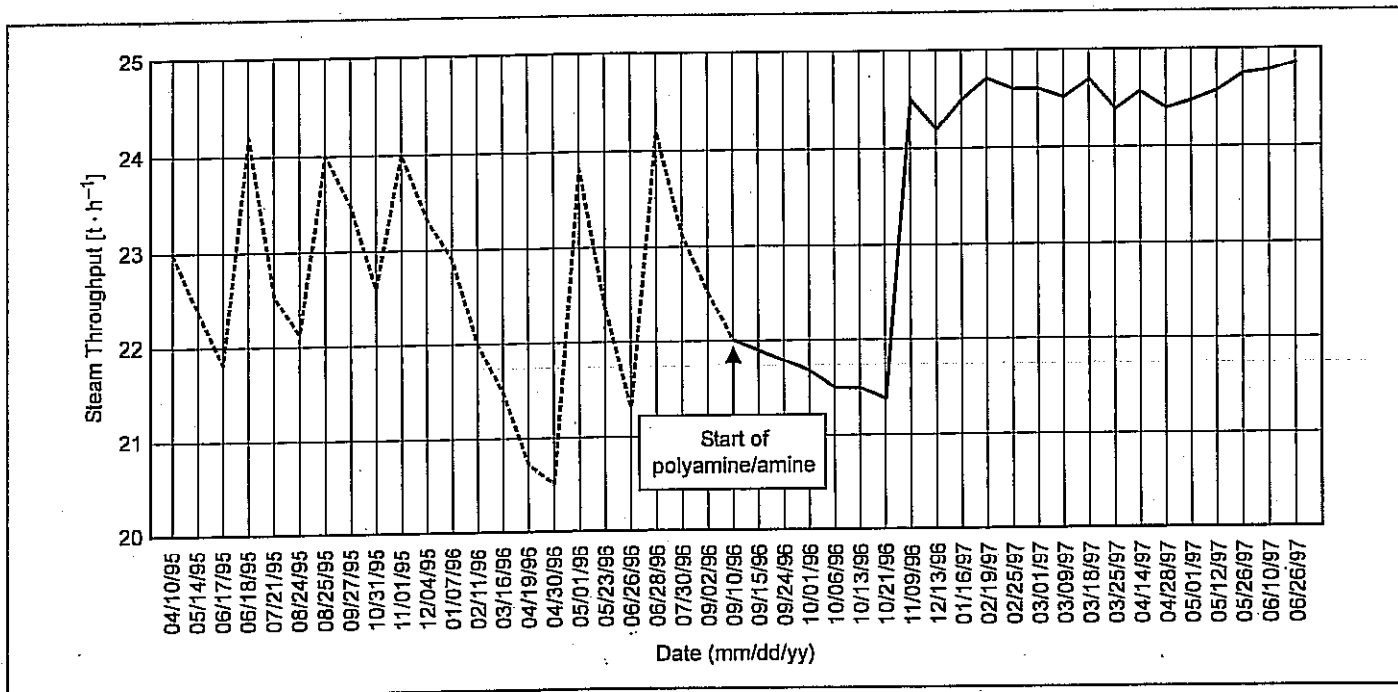


Figure 6: Steam swallowing capacity of low-pressure turbine section before and during polyamine treatment [3].

Initially, the new treatment suffered major setbacks related to dosing/mixing problems of the polyamine blend into the feedwater, and plugging of instrumentation and analytical equipment due to the "uncontrolled release of deposited iron oxides." Soon, however, the benefits of the polyamines became apparent. *Figure 6* shows the development of the turbine performance in the period before and during the polyamine treatment.

More recent data show that the turbine performance has not diminished. Turbine flushing is not necessary anymore. The turbine has not been taken out of service for inspection since 1996!

Using the on-line method described in [4], it was demonstrated that the pH difference between the first condensate and final condensate is smaller with polyamines than with ammonia. Hence, polyamines help to minimize FCC. It has also been established that the contribution of polyamine degradation products to the acid conductivity of steam is around $0.1 \mu\text{S} \cdot \text{cm}^{-1}$.

Polyamines have safeguarded the steam system's integrity during two upsets resulting from resin regeneration errors at the demineralization plant:

- a boiler water pH (25 °C) < 6 over a 3¹/₂ h period (sulfuric acid),
- a boiler water pH (25 °C) > 12 over a 4¹/₂ h period (caustic soda).

The steam system has also been operated without polyamine addition because of simultaneous failure of both dosing pumps. As a result, the boiler water pH (25 °C) remained at the lower limit (5) of the pH meter for 16 h.

Fortunately, the boiler water pH_T still satisfied the "neutral pH_T + 1" requirement.

It should be noted, of course, that contrary to the water-wall boiler of the previous case, the Lamont boiler is of a quite forgiving design without high heat flux zones and with little risk of fouling of the interior coil surfaces with magnetite.

Finally, it has been recognized that the reduced friction inside the boiler tubes allows a higher boiler water throughput, and, therefore, a higher recirculation ratio. Given the operational advantages, the polyamine treatment was not abandoned when a new water plant came on-stream supplying demineralized water with TOC concentrations lower than $100 \mu\text{g} \cdot \text{kg}^{-1}$.

CONCLUSIONS

In this paper some important differences between steam generation in the utility sector and in the chemical process industry have been discussed with particular reference to the authors' operational experience with organic compounds in the steam systems of DSM and SABIC plants in the Netherlands. High heat flux designs and operation modes susceptible to upsets make industrial HRSGs/WHBs sensitive to corrosion, especially when heat transfer surfaces become fouled with corrosion products.

The stringent water and steam quality guidelines laid down by TÜV, VGB, EPRI, etc., cannot be satisfied in many industrial steam cycles. Therefore, the approach advocated in this paper is to minimize FAC, FCC, and the formation of porous magnetite in general, in order to keep heat transfer surfaces free of deposits.

Conventional chemical treatment programs are not always successful in this respect. A polyamine program can be a worthwhile alternative. Our experience with polyamines so far has been positive and has made us confident enough to consider these products for "the next pressure level up," i.e., 12.5 MPa steam systems.

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Roy van Lier (M.Sc., Raw Materials Processing, Delft University of Technology, Delft, Netherlands, M.A.Sc., Hydrometallurgy, University of British Columbia, Vancouver, Canada) previously worked as a process metallurgist in the international mining industry on various assignments involving multiple metals, but primarily zinc. In 2001, he joined the DSM Materials and Corrosion Department. Here, he worked together with Jo Savelkoul on all kinds of corrosion and water treatment issues in various chemical plants. Most of all, however, he enjoyed working in DSM's naphtha cracker complexes, which have since been acquired by SABIC, Saudi Basic Industrial Corp. As per January 2005, Roy van Lier has been working as a corrosion specialist with the SABIC Competence Center Manufacturing in Geleen, Netherlands.

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