

Three Years of Experience with Polyamines in the High Pressure Steam System of a Naphtha Cracker

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ABSTRACT

The design and operation of the high pressure steam system of a naphtha cracker pose specific problems which in some cases cannot be satisfactorily resolved with conventional water/steam treatment programs. Following a decade of operational experience with polyamine products at lower pressures at the Geleen (petro)chemical site in the Netherlands, the ammonia/morpholine treatment of the 12.5 MPa steam system of one of SABIC Europe's naphtha crackers was converted to a polyamine program in November 2005. In this paper, the characteristics of the cracker's steam system are first described. Particular aspects of the conversion are then discussed. Finally, the experience gained and insights obtained into the polyamine treatment during the first three years are elaborated.

INTRODUCTION

SABIC Europe owns and operates three naphtha cracker complexes: two in Geleen, Netherlands and one near Teesside, United Kingdom. The UK cracker has a capacity of approximately 0.85 Mt of ethylene per annum, while the two Dutch crackers have a combined capacity of about 1.3 Mt of ethylene per year.

Although their designs and operating modes are quite different, the three plants have some general peculiarities of high pressure (HP) steam generation in crackers in common. First of all, naphtha crackers are equipped with very high heat flux transfer line exchangers (TLEs) - cracker-specific heat recovery steam generators (HRSGs) - which are susceptible to fouling and corrosion. Secondly, the design of the steam cycle is minimalistic without mud drums or large headers for collection and removal of magnetite deposits and with little instrumentation to rely on. Furthermore, the feedwater and boiler water of multiple TLEs are centrally alkalized. That leaves only the blowdown rate to adjust boiler water quality in the HP steam system of a given naphtha furnace. This is all the more challenging since TLE steaming rates vary considerably between start-up, steady state operation and decoking of the furnaces. Finally, preventive chemical cleaning of TLEs is not an option for reasons of plant availability, equipment accessibility and costs.

One of the crackers in the Netherlands, hereafter referred to as "the cracker" or "the Geleen cracker," produced its first ethylene in 1978. Its 12.5 MPa steam system was originally alkalized using ammonia, hydrazine and morpholine. The dosing of hydrazine was stopped in 1996.

For this cracker, corrosion and steam quality problems could

not be adequately resolved using conventional treatment chemicals. Following a decade of predominantly positive operational experience with polyamine products at lower pressures at the Geleen (petro)chemical site and elsewhere in the Netherlands, the treatment of the cracker's HP steam system was converted to polyamines in November 2005.

In this paper, the characteristics of the cracker's steam system are first explained in general terms. Particular aspects of the conversion are then addressed. Finally, the experience gained and insights obtained into the polyamine treatment during the first three years are elaborated.

CRACKER STEAM SYSTEMS

In a naphtha cracker, liquid naphtha feedstock is cracked into ethylene (C₂), propylene (C₃) and a whole range of light and heavy hydrocarbons at a temperature of 800 °C - 850 °C. The cracking process takes place in reactor coils in refractory lined furnaces equipped with burners. These are fired using methane produced by the cracker itself and natural gas.

Two independent and distinctly different steam systems can be distinguished in a cracker:

1. a low pressure process steam system
2. a high pressure turbine steam system

Low Pressure Process Steam System

The cracking process uses so-called dil(ution) steam or process steam to lower the partial pressure of naphtha components, and, thus, the required cracking temperature. Upon cooling this steam is condensed together with gasoline fractions. The resulting condensate is separated from the hydrocarbons either in a drum or in a tower.

The hydrocarbon-laden steam condensate subsequently proceeds to a stripper to remove as much total organic carbon (TOC) as possible through injection of clean low pressure (LP) steam. The stripped condensate becomes the feedwater for dilution steam production.

At the Geleen cracker, dil steam is produced in a battery of natural circulation HRSGs with a common drum. The boilers are vertical shell and tube heat exchangers with the boiler water on the shell side. The tube side medium is hot quench oil. Drum pressure is 0.7 MPa.

Because of elevated TOC concentrations in the feedwater, the dilution steam system has long been the subject of water quality, fouling and corrosion problems. These difficulties are partly inherent to the system in the sense that the optimal pH for aqueous/organic phase separation significantly differs from the pH for proper alkalization of feedwater. Furthermore, the required hardware (instrumentation, multiple dosing points) for adequate pH control has been lacking.

Following long operating periods with ethanolamine (ETA) and trials with sodium hydroxide for pH adjustment and an amide-based dispersant for fouling control, the dil steam system has been treated with a polyamine-polyacrylate blend since 1998. Although the process steam system is not the focus of this paper, it is mentioned here as it represents an area where a lot of site experience with polyamines has been gained.

High Pressure Turbine Steam System

As explained in previous papers [1,2], the design and operating regimes of steam generators in the chemical process industry (CPI) are dictated by the (petro)chemical process conditions. This very much holds for the HP steam system of a cracker.

Steam system description :

A block diagram of the cracker HP steam system prior to conversion to polyamine treatment is depicted in [Figure 1](#). Feedwater was — and still is — thermally deaerated at ca. 125 °C through LP steam injection. Before conversion to the polyamine program, morpholine was dosed into the suction line of the feed pumps. Hydrazine was used until 1996.

[Figure 2](#) shows how the TLEs and peripheral equipment are integrated into the cracking process. Each furnace has its own HP steam system in which one drum serves either 2 or 3 TLEs. The metallurgy of the TLEs, like the rest of the steam cycle, is all-ferrous.

All drums receive the same centrally alkalized feedwater. In other words, the only degree of freedom left to adjust boiler water quality in a given system is the blowdown rate. Blowdown is normally controlled by pH and on rare occasions by the silice concentration.

Periodically, the carbon fouling on the inner surface of reactor coils in a furnace, transition lines and cracked gas entrance to the TLEs is removed in a decoking operation. This entails the oxidation of the coke deposits using a steam/air mixture. During decoking, the steaming rate of the TLEs is reduced to approximately 40 % of normal steam production.

HP steam is superheated using hot flue gas. At the Geleen cracker, the temperature of superheated steam is controlled at 520 °C through feedwater attemperation.

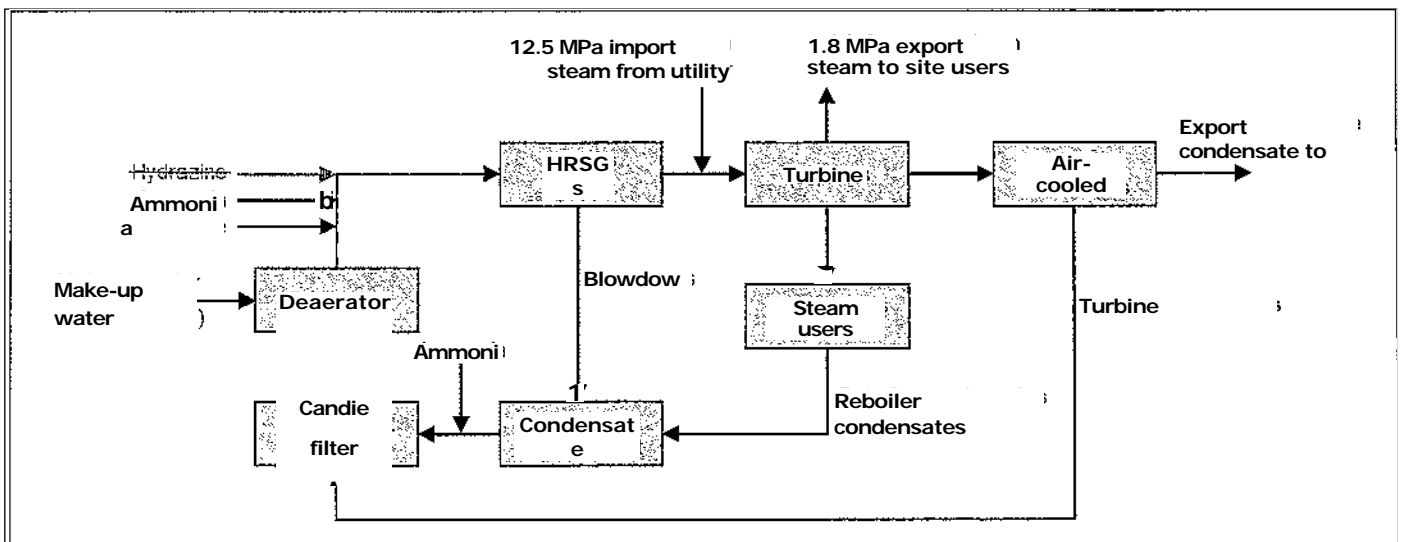


Figure 1.
Block diagram of cracker HP steam system from the mid 1990s up to conversion.

ASPECTS OF THE CONVERSION OF ANIMONIA/MORPHOLINE TO POLYAMINES

Rationale

A summary of the corrosion history of the cracker's HP steam system was presented as the "Morpholine Case" in [1]. It is repeated and elaborated here.

In essence, over the years, the HP steam cycle of the Geleen cracker has been plagued by two corrosion phenomena:

1. Flow-accelerated corrosion (FAC) in the pre-boiler and condensate systems [7]
2. First condensate corrosion (FCC) in the condensate system [8]

Both have led to the transport of iron (oxides) and subsequent fouling of thermally highly loaded heat transfer surfaces in the TLEs with porous deposits. These have acted as concentration cells for non-volatile boiler water contaminants, resulting in boiler tube failures.

Since start-up of the cracker, several measures have been taken to minimize corrosion and the transfer of iron (oxides) from the pre-boiler and condensate systems to the TLEs:

- Alkalinization of polished condensate with ammonia to combat FAC in the line from the CPU to the deaerator;
- Installation of a cartridge filter in the combined return condensate line to remove suspended iron oxides, especially from the air-cooled turbine condensates;
- Modification of the operating mode of the steam cycle from "standard" all volatile treatment (AVT) to high-AVT by increasing the ammonia concentration in the feedwater from 0.1-0.2 mg • kg⁻¹ to 1 mg kg⁻¹ in order to counterbalance loss of alkalinity due to acidic morpholine degradation products and, in this way, limit FCC;
- Discontinuation of hydrazine dosing to allow a few ppbs

of residual oxygen in the feedwater for stabilization of the magnetite layer to reduce FAC susceptibility.

Additionally, periodic operation of bottom tubesheet blow-down valves for removal of deposits from the TLEs has been strictly adhered to from the early 1980s on.

The evolution of the HP steam cycle configuration and treatment is graphically summarized in [Figures 3 and 4](#). Taking out the hydrazine dosing finally led to the layout of Figure 1.

Despite all of the modifications, difficulties with corrosion and steam quality persisted. The root cause was the thermal instability of morpholine. With more and more supporting literature on the negative effects of acidic breakdown products of morpholine, the search - at that time with DSM - for alternative steam cycle treatment chemicals was intensified in the late 1980s.

Sodium hydroxide and sodium phosphate were not considered as options since under the "wrong circumstances" (i) these may themselves become a threat to boiler tube integrity and (ii) both are prone to cause turbine fouling due to mechanical carry-over. Moreover, the use of either NaOH or Na₃PO₄ would have necessitated major hardware changes so as not to use Na-bearing water for attemperation of superheated steam.

Several organic iron dispersants were investigated via laboratory testing. Experiments were done with electrically heated steel probes in alkalinized deaerated demineralized water in a 10 L continuous autoclave at a heat flux of 100 kW • m⁻², a bulk water temperature of 300 °C and a water residence time of approximately 1 h. Tests were followed by detailed microscopic investigation of the probes and comprehensive analysis of water samples.

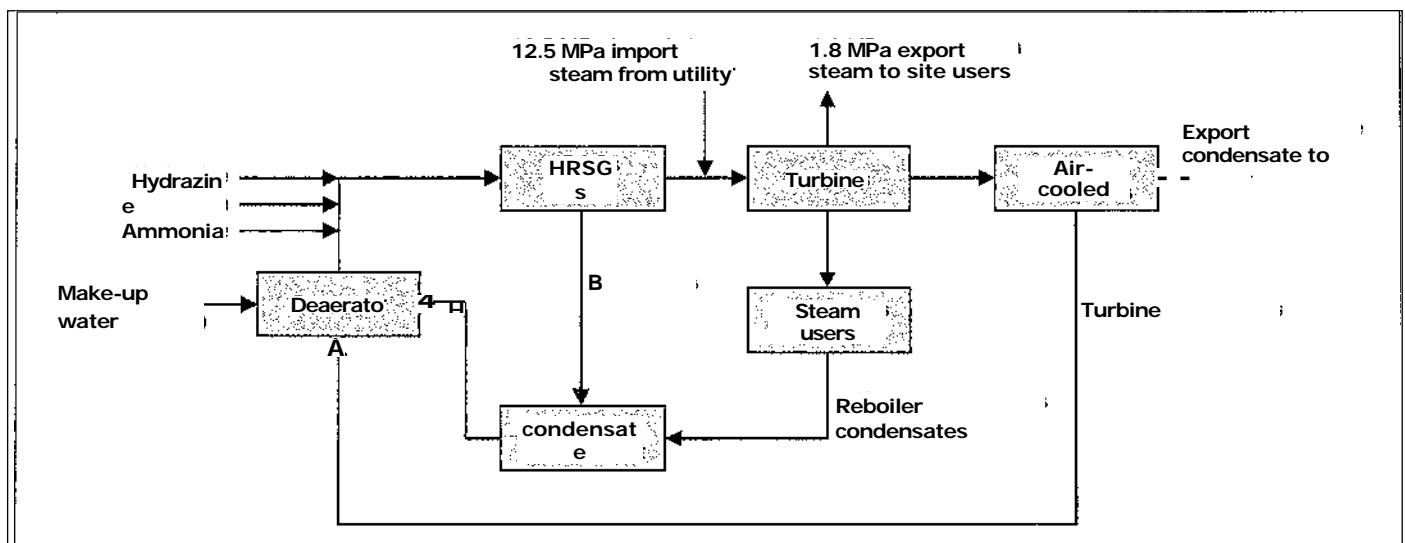


Figure 3:
Block diagram of cracker HP steam system at commissioning in 1978

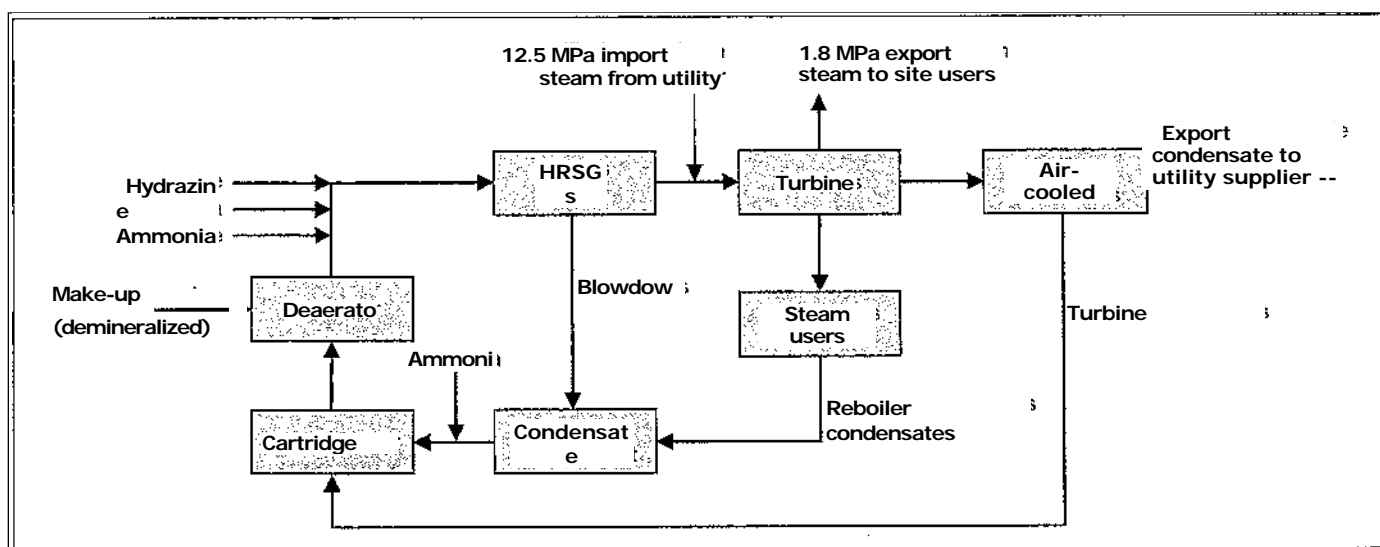


Figure 4:
Block diagram of cracker HP steam system by the mid 1980s.

Although most dispersing agents tested turned out to be unfit for use at cracker conditions for reasons of thermal degradation and/or because they did not demonstrate a clear beneficial action, one suitable candidate was identified. The continuous removal of loose magnetite deposits and complexation of dissolved iron (hydroxide) species certainly seemed to be a promising approach to the mitigation of deposition problems in the boiler systems.

A desk study was carried out to evaluate all kinds of neutralizing amines as substitutes for morpholine. This study comprised rigorous pH_T -calculations using an in-house developed computer program. With the exception of ETA, all amine alternatives were considered unsuitable for the cracker HP steam cycle because of thermal instability, lack of alkalinizing power, volatility, excessive costs, limited availability and/or insufficient operating experience.

In the mid 1990s, DSM was gaining its first site experience with mixtures of neutralizing and filming amines [1]. It was felt that the combined alkalinization and "cleaning" action of these so-called "polyamine" blends would be the key to solving the problems in the cracker's HP steam circuit and, possibly, in many other industrial steam systems. Indeed, to date we still believe that only polyamines make it possible to combat the *source* and *symptoms* of iron (oxide) transport problems integrally.

Despite encouraging test results in the lab and a successful trial run in an old 14.0 MPa power plant boiler in Geleen just before its dismantling, these new amine blends definitely needed to prove themselves in a (petro)chemical plant environment before they were to be used in a cracker. It was expected that a common interest of potential endusers, suppliers and researchers would further polyamine technology in the years to come. In the meantime, an ammonia/ethanolamine treatment was considered the next best replacement for the ammonia/morpholine alkalinization.

Some 10 years later, the cracker's HP steam system is treated with polyamines. The ETA program was never implemented. The amount of *fundamental* and *generic* data on polyamine technology available in the public domain has not significantly improved over the last decade.

Polyamine Knowledge Base

In our opinion, both the development and acceptance of polyamine technology are hindered (i) by the confidential and proprietary nature of much of the research work, (ii) by a wait-and-see attitude, or, at times, even an antagonistic position of technical institutes and major equipment suppliers, and (iii) by a fragmentation of some of the suppliers' knowledge base in recent years.

In our view, the status quo puts (potential) users of polyamine products into a difficult position: it demands a high level of expertise and analytical capabilities of the client and/or strong confidence in the supplier's know-how. It is hoped that the discussions at the Lucerne conference Interaction of Organics and Organic Plant Cycle Treatment Chemicals with Water, Steam, and Materials will contribute to changing the "polyamine position" for the better.

The advancement of polyamine technology has largely been driven by the industry. The application of polyamines has been described for a Polish power plant [9], German electrical power and co-generation plants [10-16], Belgian power plants [17-19], steam systems in the international paper industry [20-23], utility plants at a German oil refinery [24-26] and steam systems in the Swedish [20] and Dutch [1] CPI Boil-out and on-line cleaning experience with polyamine-polyacrylate mixtures in power plant boilers has been recorded in [24-26] and [19,27], respectively. Not all applications have resulted in positive results [19,28].

The problem with case descriptions is that they contain information that is not directly transferable — just like the contents of this paper. Unfortunately, little applied let alone fundamental research work on polyamines is available in the public domain, the work reported by Bohnsack [29], Frahne and Blum [30-32] and Steinbrecht [33,34] being positive exceptions. The pioneering work by Moran [35] is gratefully acknowledged. It is highly appreciated that Hater [36] utilizes pure components rather than proprietary amine blends as part of a recent BK Giuliani research project.

Thanks to Bursik's "ambassador role" [37,38], polyamines can no longer be ignored by technical institutions such as Electric Power Research Institute, Palo Alto, CA, U.S.A. (EPRI), TÜV and VGB PowerTech (VGB).

Chemistry of Typical Neutralizing/Filming Amine Blends

The Material Safety Data Sheets of several commercial formulations of polyamine products list three major components:

1. Octadeceny1-1,3-propane diamine
2. Cyclohexylamine
3. Ethanolamine

Since one of the principal concerns with these products is thermal stability, it is worthwhile considering the nature of potential breakdown products and unwanted interactions. Many problems can be prevented by selecting the appropriate amine blend and by choosing proper dosing points and equipment.

Octadecenyl-1,3-propane diamine (OPD)

This is the "mode" component" Bohnsack investigated [29]. He referred to it as N-oley1-1,3-propane diamine, a trivial name; organic chemistry purists would describe OPD as N-((Z)-octadec-9-enyl)propane-1,3-diamine. OPD is the principal filming amine in the mixture.

Possible degradation products of OPD include ammonia, carbon dioxide, short chain amines and octadecylamine. On the one hand, chemisorption of OPD onto iron oxides will enhance its thermal stability. On the other hand, such interaction will increase its retention time in the system, thus making it more amenable to breakdown.

Cyclohexylamine (CHA)

CHA is a multiple-action constituent in the amine mixture. First of all, it is presumed to have a stabilizing (possibly emulsifying) effect on the blend, particularly when dosing and diluting the polyamine product. Secondly, it is attributed a stabilizing effect on the polyamine film at the water/steel interface. Finally, due to its volatility, it is a good steam alkalization agent.

We are not completely sure about the mechanisms behind these alleged stabilizing effects. In light of this, it would also be very interesting to know what exactly goes on at the boiler water/steam interface, where CHA is preferentially released into the steam phase. How is the stability of the polyamine film affected in that area? Does alkalization at the waterline default to the neutralizing amines present in the blend?

According to Frahne, CHA may form dimers and trimers as well as components like N-cyclohexyl-1,3-propane diamine derivatives in the steam system.

Ethanolamine

ETA is much less volatile than CHA. Generally speaking, its oxygen atom is sensitive to replacement by nitrogen.

The use of ETA has come under scrutiny for reasons of the interaction of breakdown products with ion exchange resins leading to capacity losses in CPUs [39,40].

SABIC Polyamine Experience

SABIC, partly through its DSM heritage, has over 10 years of operating experience with polyamines.

Our own experience has made us especially observant of the following four polyamine related issues:

1. availability of CHA
2. occurrence of fouling
3. compatibility with catalysts and ion exchange resins
4. compatibility with site utilities infrastructure

Availability of cyclohexylamine

Figure 5 shows how we have built in flexibility to modify the CHA concentration, if necessary, in the steam system.

Questions, of course, are (i) what the appropriate CHA-to-polyamine ratio really is, (ii) how its optimal value varies within the steam cycle, and (iii) how it relates to the dosing point of polyamine into the feedwater line, where the dilution factor is in the order of 10^6 .

In our experience, to some extent, the "right" CHA-to-polyamine ratio is a matter of trial and error. For now, maintaining the pH (25 °C) of treated condensate from the CPU at > 8.5 against (erosion-)corrosion seems to work in terms of CHA availability for polyamine stabilization as well.

Although most of it is added upstream from the deaerator, CHA losses to the deaerator's steam plume are minimal. Dosing of polyamines to condensate exiting the CPU is not an option anyway since the temperature there is < 90 °C.

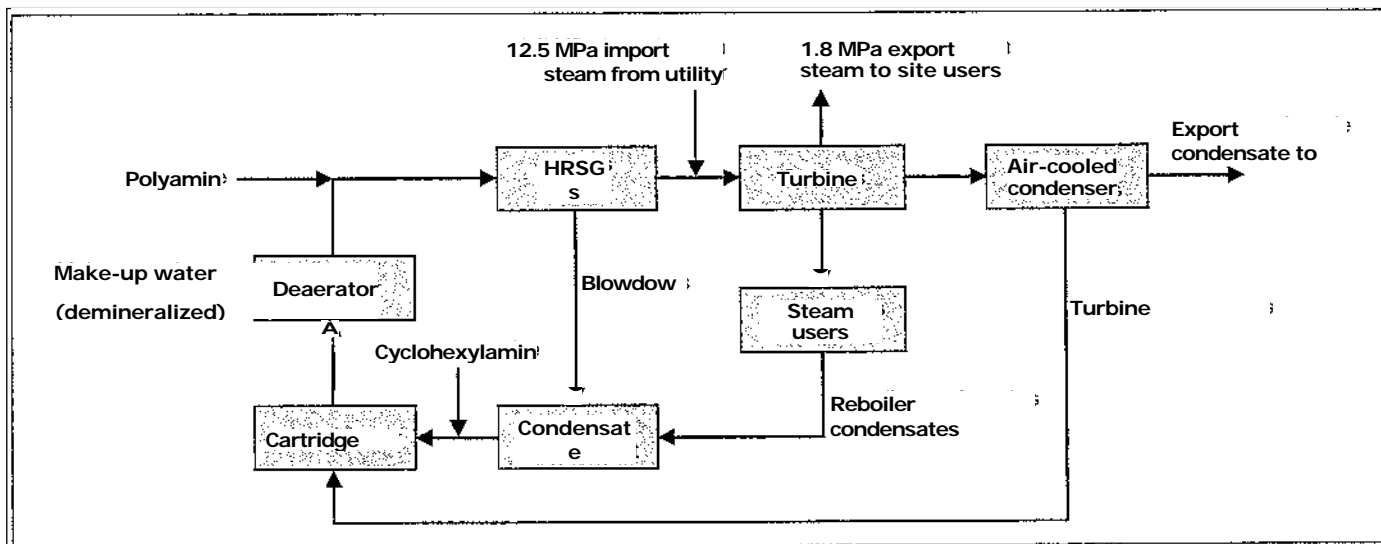


Figure 5:
Block diagram of cracker HP steam system with polyamine treatment; polyamine product also contains cyclohexylamine.

Occurrence of fouling

In our experience, polyamine-related fouling issues may be related to:

- Overdosing or locally insufficient dilution/dispersion;
- Unfavorable amine distribution ratios - with an important role for CHA;
- Thermal instability resulting in amine exchange (scrambling) reactions;
- Excessive fouling (iron oxides, organics like lubricating oil) from previous treatment/operations.

Controlled dosing is of paramount importance: operators must be trained not to increase the polyamine addition rate at the first lowering of pH values in the steam circuit.

Typical locations for deposits are strainers and small diameter instrumentation lines. The sticky nature of a fouling sample may quickly disappear upon contact with CHAI

Whereas (sticky) deposits in a HP steam system are never a pretty sight, it is important to realize that with polyamines, because of their "cleaning" effect, some degree of localized fouling is acceptable as long as the uninterrupted safe operation of the steam circuit is guaranteed. *Manageable fouling* includes, for instance, cartridge filter cakes or strainer deposits that accumulate predictably and can be periodically removed.

Compatibility with catalysts and resins

Polyamine suppliers have documentation on file on this. In general, there do not seem to be deleterious interactions between polyamine products and catalysts or ion exchange resins.

Compatibility with site infrastructure

The cracker polyamine program has been discussed with the Geleen site utility supplier and the biological wastewater treatment plant. No corrosion or fouling problems have

been reported by site users of polyamine treated steam. This is all the more interesting since there is no control over the CHA-to-polyamine ratio once the cracker export steam is put onto the 1.8 MPa grid.

EXPERIENCE TO DATE

Ammonia/morpholine containers were replaced with cyclohexylamine/polyamine units in November 2005. The initial polyamine dosing rate was kept low on purpose to assess the response of the HP steam system to the new chemicals in terms of pH, (acid) conductivity, fouling, etc. No changes were made to the blowdown regime in place at the time.

Three years later, the polyamine program has lived up to many of our expectations. As will be shown further on, the steam quality has greatly improved with respect to acid conductivity. Important water and energy savings have been realized through blowdown reduction. The time between regenerations of the cation exchangers in the cracker's CPU has more than doubled. Inspections have shown TLEs and drums to be effectively protected against corrosion by a thin, uniform, adherent, non-dusting, slightly hydrophobic magnetite layer. Turbines taken out of service for maintenance during the planned cracker shutdown of April 2007 were exceptionally clean and free of corrosion damage, although years of operation at that time is too short a period to give credit to the new treatment for this.

The (conversion to the) polyamine program has also revealed its dark side. Fouling incidents involving sticky, shoe-polish-like deposits have occurred in the pre-boiler and condensate systems. Cation exchange resin lumping

and flotation has been experienced in the CPU. One CHA container had to be replaced because of the formation of a floating layer, presumably cyclohexylammonium carbonate, through reaction between CHA and carbon dioxide in the air.

In the text below our practical experience so far is elaborated .

Feedwater Train Fouling

For reasons beyond our control, the feedwater filter was not in operation for most of the time between November 2005 and the April 2007 turnaround. During that period, due to their construction with a stagnant zone, the exiting water compartments of the feedwater heaters acted as settlers for suspended solids passing the highly turbulent deaerator ([Figure 6](#)).

The sticky nature of the deposits is indicative of an unfavorable CHA:polyamine ratio. Although the critical micelle concentration of OPD of about $4 \text{ mg} \cdot \text{kg}^{-1}$ [29] may occasionally have been exceeded, it is not believed that this has a direct relation to the fouling we experienced.

Some of the sticky deposits must have made their way into the drums and TLEs since similar fouling was also observed in blowdown flash tanks and in the CPU, where it is retained by the carbon filters. Fortunately, no indications of fouling were found during waterside video camera inspections of TLE bottom tubesheets and internal drum inspections.

This all goes to say that feedwater filtration is a prerequisite for a successful polyamine program at the Geleen cracker. The cotton fiber cartridges are now replaced once per year.



Figure 6:
Sticky deposits (most removed) and oily substances in feedwater heater.

In the period of May 2007 to May 2008, around 480 kg of cake accumulated on the cartridges. Although many of the cartridges touched, the pressure drop over the filter remained as low as 0.02 MPa.

The collected cake mass is not representative of steady state operation of the HP steam cycle in the sense that it is affected by cracker start-up after the April 2007 shutdown. It is also expected to reflect ongoing "rummaging" of older loose deposits in the air-cooled condensers. Nevertheless, it allows some order of magnitude calculations.

At 50 % moisture content and with negligible concentrations of other elements in the filter cake, whether inorganic or organic, it follows that 240 kg of iron oxide was collected over a one year period. Assuming all iron is present as (massive) hematite with a density of $5.3 \text{ t} \cdot \text{m}^{-3}$ this translates into an indicative average Fe_2O_3 removal rate of 9 μm per year for an estimated total of 5 800 m^2 internal surface area of the carbon steel air-cooled condensers.

The amount of iron contained in the cake would amount to 84 kg. Given a density of $7.9 \text{ t} \cdot \text{m}^{-3}$, this represents a carbon steel volume of a mere 10 L.

Whatever its exact nature, periodic replacement of filter cartridges makes this fouling manageable.

Feedwater, Boiler Water, Steam and Condensate Quality

[Table 1](#) provides an overview of pH values and conductivities obtained with the polyamine program compared to those in internal guidelines for the cracker's steam system.

As mentioned before, feedwater acid conductivity is measured on-line. It now typically varies between 0.10 and 0.15 $\text{pS} \cdot \text{cm}^{-1}$ as opposed to 0.15-0.30 $\text{pS} \cdot \text{cm}^{-1}$ when morpholine was used.

The acid conductivity range measured in a series of boiler water grab samples compares well with the average of about 1 $\text{pS} \cdot \text{cm}^{-1}$ for our internal reference: the boiler water of a 12.0 MPa ammonia treated system at the other cracker in Geleen.

The acid conductivity range of 0.26 to 0.47 $\text{pS} \cdot \text{cm}^{-1}$ in condensate was measured on-line as part of an investigation into the quality of the 1.8 MPa export steam to the grid. For most of the two days of testing, the acid conductivity was constant at 0.3 $\text{pS} \cdot \text{cm}^{-1}$. This is also a major improvement from the morpholine era with typically 0.6-0.7 and occasionally 1.2 $\text{pS} \cdot \text{cm}^{-1}$ or even higher numbers. The value of around 0.3 $\text{pS} \cdot \text{cm}^{-1}$ is in agreement with earlier results ([Figure 7](#)).

Parameter	Feedwater	Boiler water	Steam/condensate
pH (25 °C)			
• target range	9.0-9.5	8.5-9.5	8.5-9.5
• measured range	8.4-9.7	7.8-9.4	8.3-9.6
Specific conductivity in $\mu\text{S} \cdot \text{cm}^{-1}$			
• target range	-	-	-
• measured range	1.7-12.4	2.3-9.8	4.7-13.7
Acid conductivity in $\mu\text{S} \cdot \text{cm}^{-1}$			
• target range	< 0.2	< 3	< 0.2
• measured range	0.10-0.22	0.7-2.1	0.26-0.47

Table 1:
Summary of water/steam quality parameters.

It was determined that the TOC concentration of the 1.8 MPa steam at a fixed polyamine product dosing rate and variable CHA dosing rates ranged from 2.0 to 4.7 $\text{mg} \cdot \text{kg}^{-1}$ with pH (25 °C) between 9.5 and 9.7. In addition to CHA and filming amines the steam contained

0.5 $\text{mg} \cdot \text{kg}^{-1}$ each of ammonia (from the utility supplier's import steam) and ETA.

Interestingly, there was a discrepancy between the results obtained with Sievers 800 and Shimadzu VCPH TOC analyzers, the former giving consistently lower results. With sampling errors and the effect of time between sampling and analysis ruled out, does this leave us with a different response of polyamines to the operating principles of these two analyzers?

From the combination of the low acid conductivity of 0.3 $\mu\text{S} \cdot \text{cm}^{-1}$ and the relatively high TOC concentration of several ppms it follows that most of the organic carbon in the steam is associated with amines ("good" TOC) and little C can be attributed to organic acids ("bad" TOC). Indeed, no formic, propionic or butyric acid was detected. The reported acetic acid concentration was not credible since it would have resulted in a much higher acid conductivity. At the time of the analyses, the CO_2 content of the steam was below 0.2 $\text{mg} \cdot \text{kg}^{-1}$.

In general terms, the most unfavorable data in Table 1 were acquired just after the switch to the polyamine program with deliberate underdosing of filming amine. Stable operation was reached within weeks. Today, a pH (25 °C) of 9 is maintained throughout the system with typical specific conductivities for feedwater, boiler water and turbine condensate of 3.5 to 5, 4 to 6 and 5.5 to 7 $\mu\text{S} \cdot \text{cm}^{-1}$, respectively.

In the past 3 years, there have been incidents of overdosing of polyamine: excess concentrations of 5.2 $\text{mg} \cdot \text{kg}^{-1}$ have been reported. Over time, we have been able to decrease the variability in the free polyamine concentration range from 0.5-2.5 to typically 1-1.5 $\text{mg} \cdot \text{kg}^{-1}$ as measured via the colorimetric-turbidimetric Bengal Rosa method. We are aware that this is still rather high and leaves the steam system at increased risk of fouling. For this reason and economics, of course, a residual polyamine content of approximately 0.5 $\text{mg} \cdot \text{kg}^{-1}$ is preferred.

One of the serious shortcomings of a polyamine treatment is the fact that the targeted excess filming amine concentrations coincide with the detection limit of the current analytical methods. There is a need for an improved practical polyamine analysis.

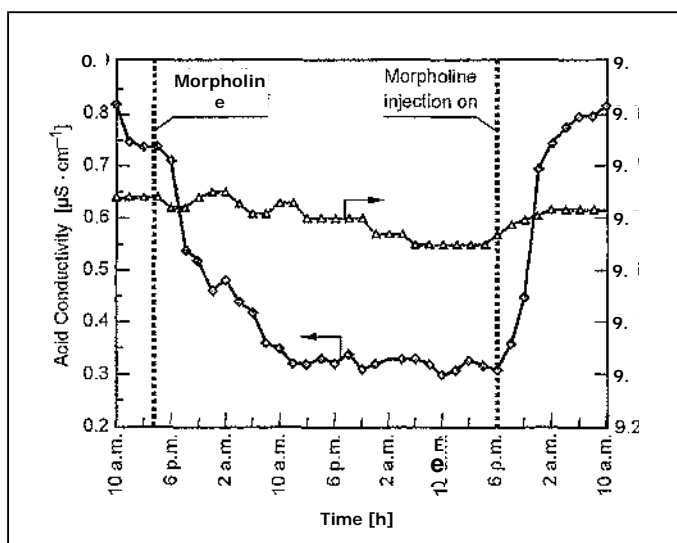


Figure 7:
Effect of morpholine dosing on acid conductivity and pH of 1.8 MPa steam [8].

Condensate Polishing Unit Issues

The polyamine program has allowed us to increase the time interval between regenerations of the cation exchangers in the CPU from 6 to 13 days. On top of considerable financial savings, fewer regenerations in the largely manually operated CPU have liberated operator time for other work in the cracker.

During start-up of the cracker after the 2007 turnaround, 3 m³ of macroporous, strongly acidic cation exchange resin had to be replaced because of unexplained lumping and flotation problems in one cation exchanger. The problem has not recurred and the performance of the cracker's CPU has been very good otherwise.

Ever since the ammonia/morpholine to cyclohexylamine/polyamine conversion, the site utility supplier treating the 1.8 MPa condensate of cracker export steam has had to double the number of regenerations of mixed bed exchangers. This seems to be due to increased carbon dioxide loading of the anion exchange resin. To date, the root cause of this phenomenon remains unclear.

The ultimate CPU related challenge would be to by-pass the cracker's condensate treatment plant under normal operating conditions. The CPU would be kept on stand-by and operated only in case of water/steam quality problems.

Blowdown Reduction

In the course of the polyamine program, the continuous blowdown of the HP steam cycle has been reduced by 75 %. This represents significant water and energy savings.

So far, the discontinuous "bottom" blowdown frequency of Borsig TLEs has not been adapted. It is expected that this ultimately will be the only blowdown required for controlling the boiler water quality between decokings. Trials with no continuous blowdown are being carried out.

Major blowdown reduction would not have been possible without the excellent demineralized water quality at our site. Indeed, our boiler water silica limit of 0.25 mg • kg⁻¹ SiO₂ is rarely exceeded, making the pH the primary blowdown controlling parameter until on-line analyzers for boiler water acid conductivity are in place.

Chemical Handling Issues

The use of a 50 % CHA solution was abandoned because the low flash point of its corresponding vapors, 34 °C, was incompatible with the ATEX zoning of the dosing area in the plant. Highly concentrated CHA solutions seem to be sensitive to the formation of a creamy cyclohexylammoniu carbonate(?) film when exposed to air.

CONCLUSIONS AND FINAL REMARKS

At one of SABIC Europe's naphtha crackers in Geleen, Netherlands, the ammonia/morpholine treatment of the HP steam cycle was converted to a polyamine program in November 2005. Three years later, SABIC experience shows that a 12.5 MPa cracker steam system can be safely, reliably and cost-effectively operated using polyamines.

The choice for polyamines has been a very conscious one based on a decade of operating experience at lower pressures, several in-house research projects and many exchanges with other users of polyamine products and suppliers.

With polyamines, the focus of the alkalization program changes from bulk water chemistry to steel/water interface chemistry. The polyamine approach is to keep boiler tubes clean from porous magnetite deposits resulting from iron transport due to flow-accelerated corrosion and first condensate corrosion in pre-boiler and condensate systems. In this way, corrosives do not get a chance to concentrate in high heat flux areas in boilers. This makes steam systems treated with polyamines more resistant to water quality upsets and - within reason - permits safe extension of the narrow bulk water chemistry operating windows dictated by EPRI, TÜV, VGB, etc.

Polyamines are no panacea. In particular, unpredictable fouling in the form of sticky oily or waxy deposits is and remains a concern with polyamine-based steam cycle treatment programs. Such fouling may result in plant "trips" due to plugging of, for instance, instrumentation lines or pump strainers. Typically, the steam system is most vulnerable to fouling problems in the early stages of the conversion phase from a conventional to a polyamine treatment program.

It is most regrettable that the public polyamine knowledge base is so limited today. It is felt that the "open ends" associated with the application of polyamines deter many potential users.

We expect EPRI, TÜV, VGB, etc., to finally accept and embrace polyamines as a credible alternative to conventional water/steam treatment programs and to incorporate polyamine programs in future guidelines. We urge polyamine users to accurately document and publish their cases. We call on technical institutes - together with suppliers - to initiate new research projects in the field of polyamine/steel interface chemistry, fouling mitigation, thermal stability and other related topics.

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