On-line Cleaning of Boilers Using A Novel Polymer Technology to Avoid Acid

Carter W. Brown[1], **Mark A. Moore**[1],
Saleh A. Al-BenHamad[1] and **Michel Didden**[2]
[1]Saudi Aramco, Saudi Arabia, [2]GE Betz, Belgium

ABSTRACT:
Periodic chemical cleaning of boilers, most commonly with mineral acids, is necessary to prevent scale build-up that results in loss of efficiency and tube failures.

Acid cleaning has to be performed during a shutdown; this increases the boiler downtime, hence increasing the cost due to lost revenue during this period. Acid cleaning also has inherent risks associated with the potential for corrosion damage to the boiler. In addition, there are also environmental issues relating to waste disposal and dangers to personnel handling strong acids.

This paper outlines a new polymer based on-line cleaning program that has been shown to be simple in operation and highly effective in removing boiler deposits. Field tests on 625 psig industrial boilers demonstrated: (1) The safe use of a new polymer in terms of corrosion, handling, application and the boiler operation in general and (2) The actual effectiveness of removing boiler deposits.

INTRODUCTION:

Chemical cleaning of boilers is a time consuming and potentially risky operation. Cleaning operations require the use of specialized contractors, and so are also expensive. Most cleaning operations involve the use of strong mineral acids such as hydrochloric acid, which, if improperly applied, can cause severe corrosion to boiler internals.

At some stage, even properly operated boilers with good water treatment programs are going to require chemical cleaning. Cleaning is necessary to restore full efficiency and prevent the possibility of tube failure through overheating and tube rupture.

Over the last two decades, demineralised water has become the preferred boiler feedwater quality. The result of this change is a change in the predominant foulant composition from hardness deposits to iron and copper deposits.

This paper outlines the use of a novel polymeric dispersant as an on-line cleaning agent for boilers. Two case histories are described. These case histories describe the on-line cleaning process employed, the precautions taken during the cleaning procedure to ensure that no internal corrosion was occurring, and the results of the cleaning procedures.

Polymeric Dispersants

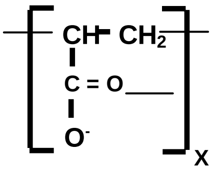
There are several polymers that are used to disperse hardness salts (calcium and magnesium) and to some extent iron. The removal of these salts from a boiler is essential for two principal reasons:

1. To prevent loss of efficiency of the boiler
2. To prevent localised overheating of the boiler tubes which leads to tube rupture (creep rupture)

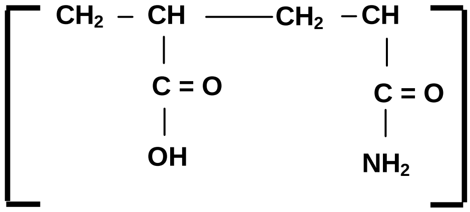
The most common dispersants are based on polyacrylate, polymethacrylate and acrylate-acrylamide copolymers. Over the last thirty years the use of softened water as boiler feedwater has declined in favor of demineralized water. The improved quality of feedwater means that the likelihood for the formation of hardness scales has decreased, while the likelihood of scaling from iron corrosion products has increased. To help counter the increasing problems due to iron scaling a well known chemical company developed a novel polymer based on an isopropenylphosphonic (PIPPA) anionic polymer for use as an iron dispersant in high temperature, high pressure boilers. This molecule is particularly suited to the removal of iron deposits. However, the polymer should not have any chelating properties. Chelating or suspect chelating agents are forbidden to be used in the plant.

An advantage of the PIPPA polymer is that it releases some ortho-phosphate from the phosphate radical group off the polymer chain. The ortho-phosphate would then form a chemically stable iron-phosphate particle should any soluble iron be present next to the chemically stable iron oxides solids. . The chemical structure of PIPPA polymer and some of the more conventional dispersants is shown in Figure 1.

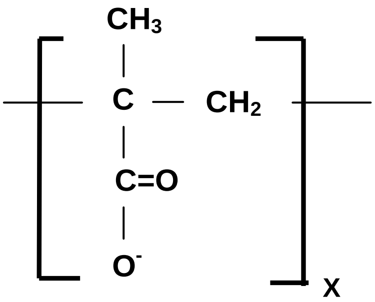
Figure 1 Polymeric Dispersants



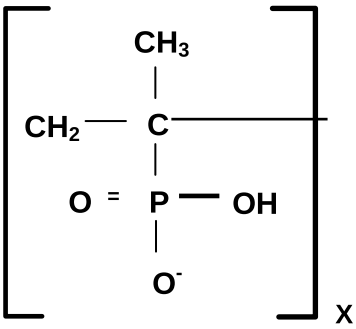
POLYACRYLATE



ACRYLATE-ACRYLAMIDE COPOLYMER



POLYMETHACRYLATE



PIPPA

The polymer was first developed as a continuously injected treatment program. However, one petrochemical plant in the United States tested the polymer for on-line cleaning of boilers with some success. The high risk of corrosion in using acid to clean a boiler provided a strong basis to consider the polymer for an on-line cleaning trial.

Case Histories

Both boilers that were on-line cleaned were of the same design. These units are “D”-type water tube boilers, of 530,000 lbs/hr maximum load, operating at a pressure of 625 psig.

Boiler F-103

Procedure

Boiler F-103 was the first boiler in which the on-line cleaning was to be attempted. The total period available for the on-line cleaning was eight weeks. It was decided to take a gradual approach to the addition of the polymer, starting with 5 ppm of PIPPA for a period of two weeks and increasing the level by 5 ppm increments every two weeks until a maximum of 20 ppm was present. The reason for this gradual approach was so as not to remove too much loose iron deposit on first introducing the polymer to the boiler and hence risk plugging blowdown lines. During the time that the level of PIPPA was being increased, the use of the normal dispersant (carboxylated methacrylate - CMA) was continued, although at decreasing levels, in order to maintain the desired phosphate level in the boiler.

The principal route through which iron is removed from this design of boiler is through the bottom (intermittent) blowdown. In order to help in the removal of iron from the boiler, the frequency of the intermittent blowdown was increased from once per day to once per shift. Blowdown practice was continued as recommended by the boiler manufacturer.

A further way to aid in the removal of iron from the boiler is to decrease the boiler cycles of concentration (COC). Boiler F-103 is usually operated at between 80-100 cycles. During the on-line cleaning procedure F-103 was operated at ~50 COC, and the boiler was operated at a fixed load of 400,000 lbs/hr. In order to make control of COC easier, an inert tracer (a molybdate salt) is added to the PIPPA. Measuring the level of molybdate in each batch of the feedwater treatment, the injection rate of the batch, and the boiler blowdown molybdate enables the COC to be calculated. Knowing the COC allows adjustments to be made to the blowdown valve to keep the COC on target if necessary.

It is well known that certain polymers (e.g. acrylate-acrylamide co-polymers) have chelating properties and can, under the right water chemistry conditions, cause corrosion in boilers. Possible corrosion by chelation was an initial concern with the PIPPA polymer. Since iron is expected to be removed by the polymer, the use of iron monitoring of the continuous blowdown to give a measure of internal corrosion will not work. Instead, hydrogen measurements were performed on the saturated steam. An on-line hydrogen analyzer was connected to the saturated steam sample point. Measurement of hydrogen level commenced six days prior to the start of the trial to establish a baseline, then measurements were continued for the duration of the trial.

Results

The relative amounts of PIPPA during the trial period are shown in Table 1. It can be seen from this table that the overall control of the dosage rates during the trial period was very good. Control of cycles of concentration was also excellent. Table 1 also shows the averaged COC during each week of the trial. The results were between 45 and 50 cycles, very close to the original target of 50. An example of how the COC was calculated based on molybdate level is shown below.

Table 1 Relative Amounts of PIPPA during Cleaning of Boiler F-103

Week	Average PIPPA PPM Level	Cycles of Concentration
1	3.01	47.50
2	2.99	46.38
3	3.96	50.12
4	6.91	47.53
5	8.79	49.62
6	11.63	42.38
7	12.00	52.20
8	12.05	53.57
9	12.33	51.27

COC Determination

For F-103 for the period Dec 1 to Dec 21

Average molybdate concentration in batch = 145 ppm

Feed rate = 250 ml/min = 15 l/hr
Amount of molybdate entering boiler = 145 * 15 = 2,175 mg/hr

Average molybdate in blowdown = 0.57 ppm

Blowdown rate = 2175/0.57 = 4103 l/hr ~1,000 gallons

Average boiler feed rate = 395,100 lbs hr ~ 47,000 gallons/hr

COC = boiler feed rate/blowdown = 47000/1000

~ 47 cycles

Iron Levels & Hydrogen Measurements
The iron level from the continuous blowdown was measured on a daily basis, and the results are shown in Figure 1. The first four weeks data shows the iron levels before the introduction of the PIPPA, and so can be considered as a baseline. Since the boiler was operating at 100 COC at that time, the results have been corrected to 50 COC for direct comparison with the results during the trial period. It is apparent from Figure 1 that the iron levels increased shortly after the introduction of the PIPPA. That the increase in iron was not due to internal corrosion was confirmed by hydrogen measurements. Figure 2 shows the variation of hydrogen versus time. The first six days results were for the boiler operating on the normal CMA polymer water treatment program. After six days injection of PIPPA began. Hydrogen levels fell during the trial. There were

occasional spikes, the reasons for which are not known, but overall the trend was for a decline in hydrogen level, showing that the polymer was not causing internal corrosion during the cleaning process. Since the extra iron was not being generated by corrosion, it had to be due to the removal of iron deposits. The amount of iron removed could not be determined, as it is not possible to obtain samples from the intermittent blowdown, and so it is impossible to perform a full mass balance for iron across the boiler.

Post-Shutdown Inspection

Following the boiler shutdown, a visual inspection of the boiler internal condition was performed, and boroscoping of the tubes was also conducted. Visually, the boiler appeared to be clean. Some slight reddish discoloration was seen in the steam drum (especially in the vapor space), indicating some reversion of magnetite to hematite. However, some reversion of magnetite to hematite is normal, and the main intent of this on-line cleaning was to reduce the overall scale loading of the boiler, not to achieve a high level of passivation.

A screen tube was cut out of the boiler and the scale density determined. The results of the scale density measurements are shown in Table 2. The results in this table show the scale density values measured in 2000, and in 2002, following the on-line cleaning. The results are interesting, in that it seems that the greatest reduction in scale was on the cold-side, where a reduction from 538 g/M^2 to 161 g/M^2 was achieved. By contrast, the hot side scale density remained effectively unchanged at ~540 g/M^2. Although unchanged the Scale Density does show that the PIPPA has removed any deposits that have accumulated during the period 2000 to 2002.

Table 2. Scale Density Results for Boiler F-103

Date	Scale Density Hot Side	Scale Density Cold Side
2000	538 g/M^2	533 g/M^2
2002	540 g/M^2	161 g/M^2

During the shutdown period additional non-destructive examination of the tube condition was performed by remote field eddy current (RFEC) and submerged tube ultrasonic testing (IRIS – internal rotatory inspection system) techniques. These techniques can be used to determine the extent of corrosion in boiler tubes. As the techniques employ a probe which is inserted into the boiler tube, they allow examination of the main bank tubes, which is not possible with conventional ultrasonics. No tube thinning was detected, which is in agreement with the hydrogen study results showing that the polymer does not cause corrosion in the boiler.

Boiler F-105

Procedure

Based on the experience gained from the on-line cleaning of Boiler F-103, it was decided stop the CMA program thirty (30) days prior to a shutdown and switch completely to the PIPPA program for that time period. The iron levels from the boiler were measured as in the cleaning of F-103, but no hydrogen study was performed.

Results

The relative amounts of PIPPA added during the trial period are shown in Table 3. Once again, very good control of target levels was achieved during the cleaning operation.

Table 3 Relative Amounts of PIPPA during Cleaning of Boiler F-105

Week	Average PIPPA PPM Level	Cycles of Concentration
1	13.25	36.81
2	13.98	26.72
3	13.10	42.54
4	12.97	40.28

Visual and boroscopic examination of the boiler drums and tubes during the shutdown period showed that the waterside surfaces were reasonably well passivated and appeared to be clean. This observation is backed up by the scale density results for a screen tube sample. The results are shown in Table 4. These results clearly demonstrate that the overall scale density in the boiler has been significantly reduced.

Table 4 Scale Density Results for Boiler F-105

Date	Scale Density Hot Side	Scale Density Cold Side
2000	380g/M^2	
2002	80g/M^2	86g/M^2

Discussion

Comparison of on-line and off-line chemical cleaning

From the results shown in the two case histories it is clear that PIPPA can be used effectively for on-line cleaning of boilers. However, it is not going to be able to replace chemical cleaning completely. For example, pre-commission cleaning by alkaline boil-out or citric acid cleaning is still recommended. Furthermore, the use of PIPPA is restricted to the cleaning of boilers where iron scales predominate. If appreciable hydrocarbon, copper, hardness scales or silica scales are present then an off-line cleaning would be more appropriate.

In the cases where iron scales are the major contaminant in the boiler, then PIPPA has significant advantages over off-line cleaning. These advantages are as follow:

- No boiler down time
- Non-corrosive to the boiler
- Cheaper than off-line cleaning

Conclusions and Recommendations

The two case histories presented here clearly show that PIPPA is effective in performing on-line chemical cleaning of boilers, at least for those boilers where iron is the predominant component of the scale.

One option for further investigation is the use of PIPPA for a few weeks prior to every routine boiler shutdown (two to three year intervals). By such means it should be possible to eliminate the need for any off-line boiler cleaning.

Acknowledgements

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Figure 2 Iron Concentrations in Blowdown F-103 Boiler vs. Time

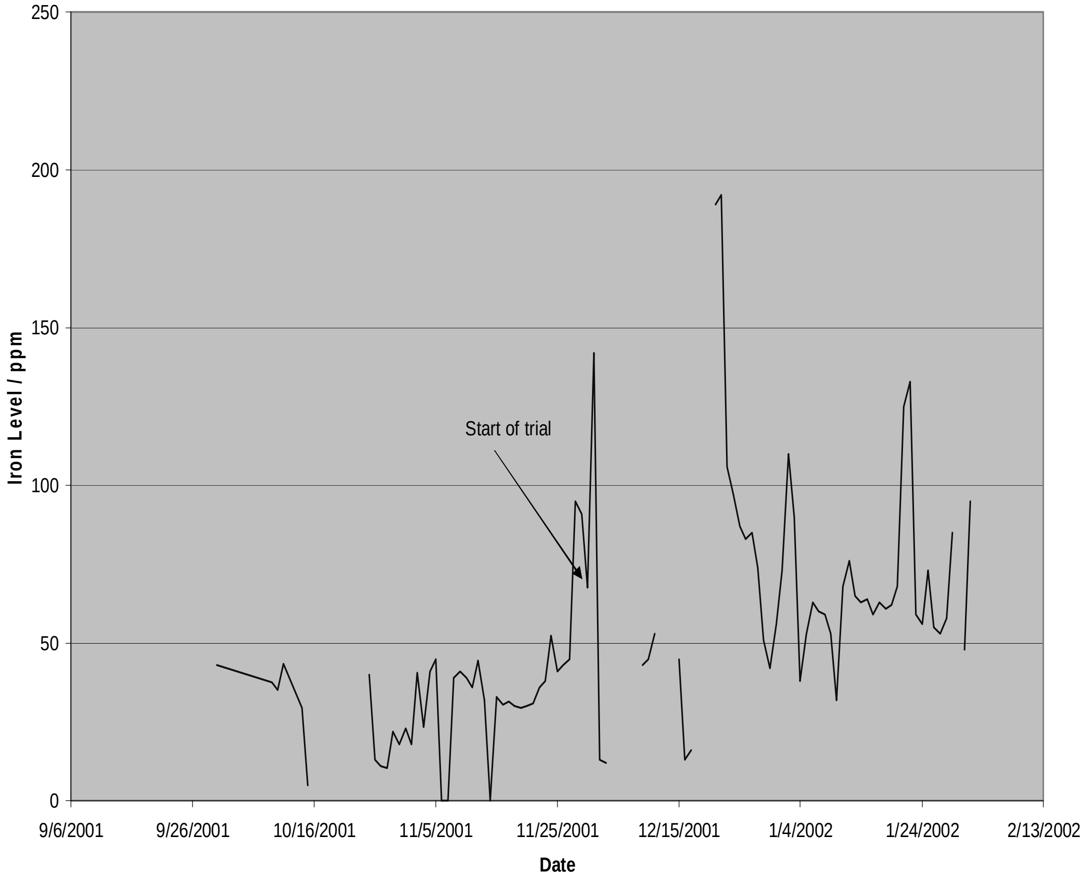

Figure 3 Hydrogen Study – First 130 hours with Normal CMA Program
Remaining Time with PIPPA Program