Field experience with a new high-temperature polymeric dispersant

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ABSTRACT: The paper industry's move toward higher boiler operating pressures prompted development of a patented high-temperature dispersant, HTP-2™. The dispersant was tested at 1450 psig, with excellent iron-dispersing capabilities. Tests in the research laboratory also confirmed that the polymer does not adversely impact steam purity or boiler corrosion, nor does it participate in any deposit-forming reactions. Field data in boilers operating from 300 to 1500 psig confirmed the research findings. From package boilers to critical black liquor recovery boilers, the field results have demonstrated superior deposit control capabilities. This new polymeric dispersant represents a significant breakthrough in high-pressure boiler waterside deposit control. The deferred costs of possible chemical cleaning, lost production, and/or personnel injury as a result of deposit-related failures, as well as the knowledge that up-to-date and proven technology is available for steam plant operators, makes HTP-2 a viable alternative to existing polymeric dispersants.

KEYWORDS: Boilers, chemical treatment, deposits, dispersants, high pressure, iron compounds, polymers.

Background

Boiler tube failures due to waterside deposits can be catastrophic. Repair costs and lost production can total thousands of dollars per day. Any waterside deposit has an impact on heat transfer efficiency and can lead to failures due to under-deposit corrosion or overheating. Steam generation reliability and efficiency is directly tied to paper production and to the overall economics of the mill. These facts, and personnel safety, make waterside deposit control a primary concern in all paper mill boiler system water treatment programs.

Paper industry trends in recent years have favored boiler operating pressures above 900 psig in most systems. This trend is related to cogeneration emphasis as well as mill-specific steam balance demands. The trend is illustrated by **Table I,** showing boiler design pressures of the past ten greenfield kraft mills built in the United States. Note that only one mill was designed to operate below 900 psig.

Synthetic polymeric dispersants have been used since the mid-1950s to control boiler waterside deposition. The results have been variable, primarily due to the variability of application technology and the quality of the boiler feedwater being treated. Early concerns regarding the control of hardness scale (hardness was the dominant contaminant) have gradually given way to the current emphasis on metal oxide deposit control, particularly control of iron deposits. Iron (and in some systems, copper) is now the dominant contaminant considered in high-pressure boiler systems, primarily due to the trend of maximizing condensate return and using demineralized water for feedwater makeup.

Betz Laboratories conducted significant research to develop an iron-specific polymeric dispersant for use in high-pressure boiler systems. This research effort represents over 12 years of laboratory development work. One result was the development of a unique patented polymer, Betz HTP-2.

Polymer chemistry

Iron oxides transported into the boiler are typically amorphous. They have a slightly positive charge with a large

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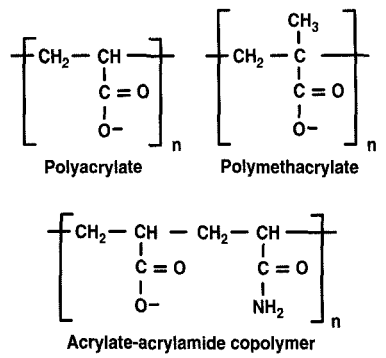
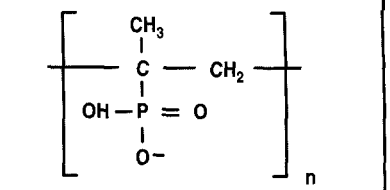
1. Paper industry greenfield kraft mill construction

U.S. mill location	Year of startup	Design boiler pressure, psig
Northeast	1976	1050
Mid-south	1977	900
Southeast	1977	1250
Southeast	1977	1175
Mid-south	1981	900
Southeast	1984	1500
Mid-south	1984	1300
Midwest	1986	600
Southeast	1990	1200
Mid-south	1990	1500

1. Polymer functional groups



2. HTP-2 functional group



surface area. These charges are neutralized by the anionic charge of the polymers, and the particulates are dispersed due to the continued dominance of the negative charges on the "sequestered" particles. Polymers are surface-active to particulate matter as well as the boiler tube surfaces. Polymer adsorption onto the metal occurs, and the negatively charged polymers adsorbed on the boiler steel surface further repel the sequestered and negatively charged particles in the bulk boiler water.

All the polymers previously available for boiler waterside deposit control were designed to handle metal oxide intrusion through the dispersion mechanism described above and then to transport them out of the boiler in the blowdown. Most of these polymers, available for many years, were originally developed to control hardness scale in the lower pressure environments of the 1950s.

Figure 1 depicts the most common polymeric dispersants used in boiler water deposit control. These dispersants are anionic and include polyacrylate (PAA), polymethacrylate (PMA), and a polyacrylate-acrylamide copolymer (PAM). The carboxylated polymers (acrylate family) have proven most effective in iron oxide dispersion in low- to medium-pressure systems.

As boiler pressures and temperatures increase, the functional groups depicted in Fig. 1 begin to lose effectiveness. In higher pressure environments, polyacrylate tends to break down (decarboxylate) to smaller and less effective units, and carbon dioxide is produced during this breakdown. Polymethacrylate also decarboxylates at higher pressures, though to a much lesser extent than polyacrylate. The superior stability of methacrylate is commonly explained by the stabilizing impact provided by the methyl group found on the methacrylate polymer.

The acrylate-acrylamide copolymer functional group tends to revert to polyacrylate and evolve ammonia when exposed to high temperatures and alkaline boiler water environments. This can be especially troublesome in mills where copper or copper alloys exist in the steam/condensate systems. Serious copper corrosion and copper-bearing boiler deposits can result. Furthermore, the polyacrylate complex produced as a result of the acrylamide breakdown can precipitate, especially in the presence of high calcium concentrations. The resultant calcium-polyacrylate deposit is extremely insulating and difficult to remove from heat transfer surfaces.

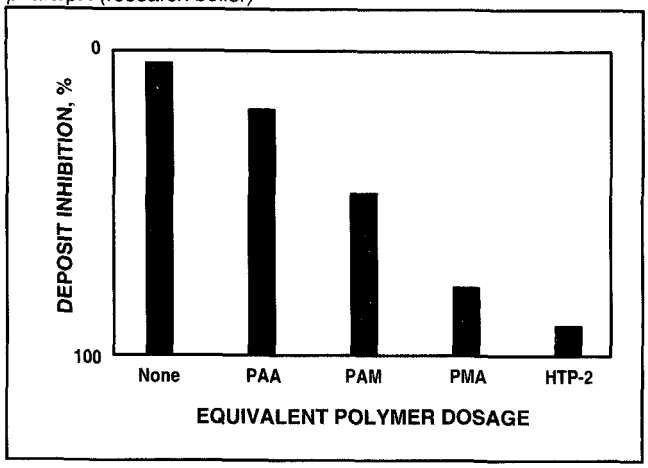
These shortcomings of the common dispersants, plus the basic need for overall improved performance at higher pressures, were the driving forces behind the Betz research effort in developing HTP-2. The HTP-2 polymer functions in the same manner as those previously described: dispersion and charge neutralization. However, the difference between HTP-2 and other polymeric dispersants lies in the functional group utilized, a modified phosphate chemistry. **Figure 2** illustrates this unique feature of HTP-2.

In contrast to the acrylate family of dispersants, the slight functional group breakdown of HTP-2 does not affect iron deposit control. A small and predictable amount of orthophosphate residual results. The amount of dephosphorylation is self-limiting (i.e., dependent on system pressure). The predictability of the phosphate contribution provides an excellent "tag" for determining the amount of polymer in the boiler system. The phosphate contribution to the boiler water is accounted for in the feed formula for the dispersant and often allows operation within the coordinated phosphate/pH control envelope without supplemental phosphate feed.

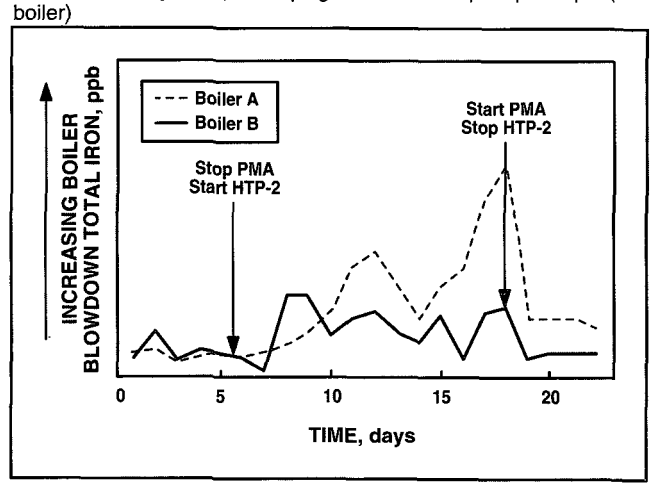
Laboratory research results

The final proof of any polymeric dispersant effectiveness is performance. Polymer performance is measured by inhibition of deposits under boiler operating conditions. This performance criterion can best be quantified using deposit weight measurements under controlled conditions. Since controlled conditions are best maintained in a laboratory environment, initial HTP-2 deposit control data were developed in the Betz Laboratories research facility in Trevose, PA. This work was done

3. Boiler deposit weight densities, 1450 psig—coordinated phosphate/pH (research boiler)



4. Boiler iron rejection, 1200 psig—coordinated phosphate/pH (field boiler)



in a 1450-psig research boiler, simulating field conditions.

Figure 3 illustrates the relative ability of various polymeric dispersants to inhibit deposition, measured by deposit weight density comparisons in a research boiler. Note that polymethacrylate is the superior performer of all the acrylate-based dispersants. However, it is evident from this chart that HTP-2 is far superior to any of the other common boiler water dispersants in maintaining deposition-free boiler heat transfer surfaces.

Providing good deposit control without regard for other aspects of overall boiler water treatment is, of course, unacceptable. Therefore, while in the controlled research environment, various testing was performed with HTP-2 in the system. In all tests, the use of HTP-2 did not impact steam purity, and no corrosion occurred. There were no damaging polymer decomposition products nor was there evidence of any polymer-based deposition. The absence of corrosion, steam purity problems, and polymer-based deposits confirm the acceptability of HTP-2 as a high-pressure boiler water dispersant.

In all research tests, HTP-2 was far superior to other boiler water dispersants. No detrimental impact from HTP-2 use was seen on any research tests or any subsequent field tests. Field experience was as positive as the research data.

Field data

Dispersant blends featuring Betz HTP-2 have been used in field boilers since early 1986. To date, more than 40 boiler systems are using HTP-2-based dispersant technology. The systems range in pressure from 300 psig to 1500 psig, and the boiler configurations include cogeneration units, utility units, chemical plants, and several paper industry power and recovery boilers. This section provides examples of HTP-2 performance in field boilers. The examples represent distinctly different high-pressure boiler systems with differing boiler designs, load swings, and operating demands.

Figure 4

Figure 4 data represent two 1200-psig paper mill boilers on the same feedwater system. The boilers used coordinated phosphate/pH internal chemistry and a polymethacrylate-based dispersant. Results were satisfactory, though not spectacular. Some iron-rich deposition was present.

The introduction of HTP-2 had an immediate and dramatic impact as seen on the graph. Boiler blowdown total iron levels steadily increased until settling at approximately twice the level achieved using the polymethacrylate dispersant. This final level of blowdown iron with HTP-2 in the system approximated a 100% iron rejection rate (i.e., the amount of iron entering the boiler equalled the amount leaving). When the HTP-2 feed was discontinued and polymethacrylate was re-applied, blowdown iron levels decreased to near the original level.

Figure 5

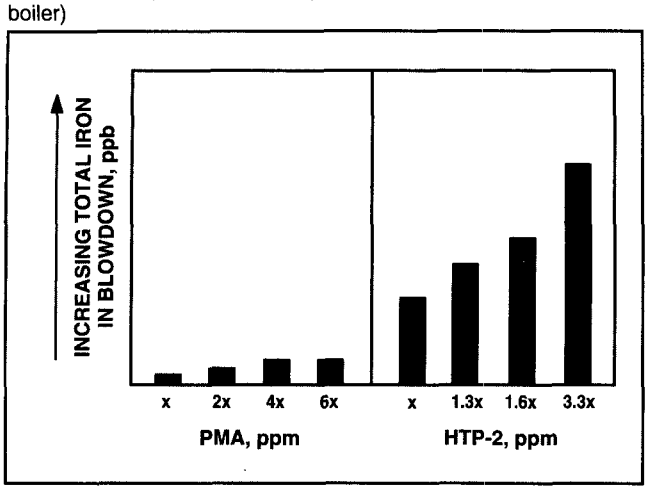
Figure 5 demonstrates the superior performance of HTP-2 vs. polymethacrylate in an ammonia plant boiler operating at 1500 psig. This unit also had a history of iron-rich deposits on the polymethacrylate-coordinated phosphate/pH treatment program. Plant operating personnel wanted to minimize further deposition and to clean some of the existing deposition, if possible.

The graph shows the dramatic impact of HTP-2. The relative dosages of polymer are normalized with the x value equal in all cases. Note the superior iron rejection achieved using HTP-2.

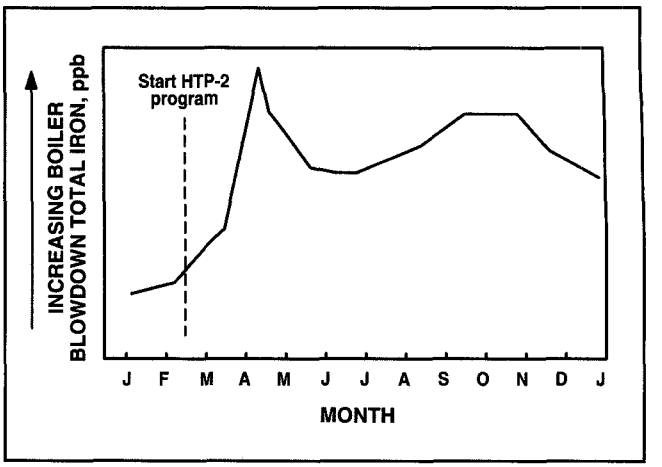
Figure 6

Figure 6 presents data developed in a 1000-psig paper mill boiler using a coordinated phosphate/pH program and HTP-2 as a dispersant. The graph shows the apparent cleanup performance of HTP-2 in the early application stages. The May/June time period decline in boiler blowdown iron represents a period of excessive blowdown due to operational problems. However, in the July/August period, iron leaving the boiler in the blowdown stabilized

5. Boiler iron rejection, 1500 psig—coordinated phosphate/pH (field boiler)



6. Boiler iron rejection, 1000 psig—coordinated phosphate/pH (field boiler)



at approximately 100% of the feedwater iron entering the system.

Annual tube sample deposit weight density (DWD) values in this system have slowly risen over the past years (using polymethacrylate dispersant). However, recent DWD values with HTP-2 in the system indicate this trend has reversed. The last series of tests showed no change from previous year values; in one case, a slight drop in DWD was recorded.

DWD is used in research boilers due to experimental design that includes frequent shutdowns. DWD is also used in the field, where the owner/operator is willing to sacrifice tubes. However, DWD testing can only be done during outages, while iron testing can be done daily. Thus, iron indicates real-time performance without downtime or destructive testing.

Summary

The patented HTP-2 polymer provides superior performance in dispersing iron under high-pressure boiler conditions. The outstanding performance of this patented material was established in controlled laboratory experiments. Performance was also confirmed in field applications in several U.S. and Canadian boiler systems, including power boilers and black liquor recovery boilers in the paper industry.

This unique polymeric dispersant represents a significant breakthrough in high-pressure boiler treatment, where iron deposition is a threat; it is a perfect fit for most paper mills. The treatment program costs are more than offset by the deferred cost of chemical cleanings, lost production, and/or personnel injury resulting from deposit-related failures. The powerhouse operator finds an attractive return on the chemical treatment investment as well as the knowledge that up-to-date and proven technology is being applied in the powerhouse systems. ■

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