

Advancing Copper Corrosion Control: Impact on Biological Wastewater Treatment Compared with Traditional Triazole-Based Inhibitors

ABSTRACT

Triazole-based corrosion inhibitors are used throughout the semiconductor industry to protect copper components of critical cooling water assets. Benzotriazole (BZT), tolyltriazole (TT) and chlorinated tolyltriazole (CI-TT) are among the most common in these applications. However, triazoles are hazardous to aquatic life when discharged directly to rivers, and harm nitrifying biomass when discharged to biological treatment systems. Nalco Water’s 3DT398, a patented¹ yellow-metal corrosion inhibitor, offers a robust solution, providing highly effective corrosion protection while demonstrating lower aquatic toxicity and minimal impact on nitrifying bacteria. This paper details the laboratory nitrification inhibition studies, field trial results, and the environmental benefits of adopting 3DT398 in semiconductor cooling towers.

BACKGROUND

Chillers play a critical role in the semiconductor manufacturing process because they remove heat from the process cooling water (PCW) loops that directly support the production process. Copper and its alloys are the most common metals used in heat exchangers found in industrial chillers. These metals are prone to corrosion, especially in the presence of oxidizing biocides including bleach and bromine.² Copper corrosion is typically controlled by adding triazole-based corrosion inhibitors into cooling water, including benzotriazole (BZT), tolyltriazole (TT) and chlorinated tolyltriazole (CI-TT).

In addition to protecting critical assets, semiconductor manufacturers must also minimize the impact of waste cooling water (blowdown) on the environment. The environmental impact of triazole-based corrosion inhibitors is an emerging concern in the industry, as they are known to be toxic to aquatic life³ when directly discharged and have a negative impact on nitrifying bacteria critical to the operation of biological treatment systems.^{4,5} This toxicity is especially problematic for the semiconductor industry because triazoles also enter the waste stream from manufacturing processes such as chemical mechanical planarization. As growth in semiconductor manufacturing volume and complexity generates even more triazole-containing wastewater, the need for a non-triazole copper corrosion inhibitor becomes even more pressing.

Nalco Water’s 3DT398 is a patented¹ corrosion inhibitor that has been shown to provide more robust yellow metal corrosion protection than the triazole-based copper corrosion inhibitors commonly used in the industry.⁶ 3DT398 also has lower aquatic toxicity than traditional triazole-based inhibitors, as shown in Table 1.⁷ Based on these results, we hypothesized that 3DT398 may also be less harmful to nitrifying bacteria used in biological treatment systems, while improving corrosion protection of critical chiller assets. In this paper, we present laboratory nitrification inhibition studies and field trial results comparing 3DT398 to three common triazole-based inhibitors.

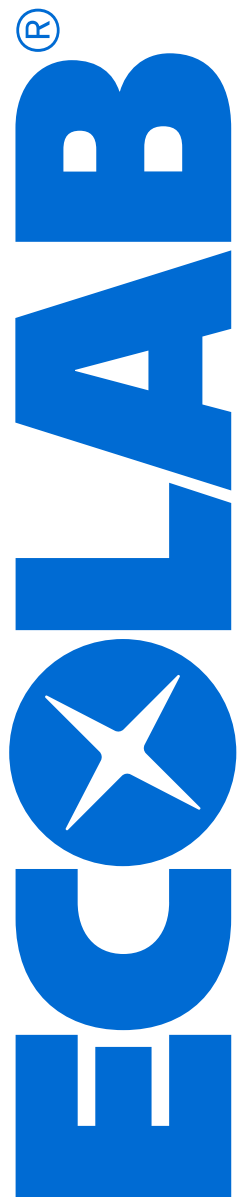
INHIBITOR	ACUTE TOXICITY FISH (LC50, ppm)	ACUTE TOXICITY INVERTEBRATES (LC50, ppm)	GHS RATING (Global)
Chloro-TT	15.4	47.4	Harmful
TT	23.7	245.7	Harmful
BZT	75	277	Harmful
3DT398	480	367	Nontoxic

Table 1: Toxicity testing for common triazole-based corrosion inhibitors vs 3DT398 (LC50>100ppm is non-toxic)

RESULTS

Nitrification Inhibition

The effects on nitrification of commonly used inhibitors compared to our new corrosion inhibitor, 3DT398, was evaluated by a third-party lab⁸ by measuring the nitrifying activity of a biomass population taken from a customer’s receiving municipal wastewater treatment facility in the state of New York. The biomass was incubated with municipal influent, 50 ppm ammonium chloride, and various concentrations of the corrosion inhibitors. Nitrification activity was calculated in terms of NO₃-N generation of each sample vs. control. The data summarized in Figure 1 clearly show that while triazole-based inhibitors have significant impact on



nitrification at concentrations as low as 1 ppm, there is no measurable effect from 3DT398 even at 25 ppm, five to ten times (or more) than typical cooling tower treatment concentration. These results show that cooling tower blowdown containing 3DT398 can be discharged to the biological treatment system intended to remove $\text{NH}_3\text{-N}$ without impacting the health of the biomass.

Field Trial Results in Semiconductor Cooling Towers

After confirming that 3DT398 would not negatively impact nitrification in the receiving biomass, we were able to begin field trials in semiconductor fab site cooling towers. Trials were completed at several customer locations under a wide range of climate conditions and make up water qualities. At all trial sites, the incumbent triazole-based corrosion inhibitor was replaced with the same actives dose of 3DT398 on large cooling tower systems and the program was evaluated for a three-month period during peak load. Copper corrosion performance was monitored on line using a linear polarization-resistance (LPR) meter before, during, and after the trials and was also verified via copper coupon analysis.

A representative LPR data set from one of the trial sites is shown in Figure 2. While copper corrosion was well controlled with BZT, the corrosion rate steadily decreased after the switch to 3DT398. After the 90-day pilot, this set of cooling towers continued to use 3DT398, and the corrosion rates stayed below the detection limit of the LPR meter. This was confirmed by copper coupons, which reported a corrosion rate of <0.1 MPY for the duration of the trial. Similar results were achieved at other sites.

The data in Figure 2 is due at least in part by improved process control after the change from BZT to 3DT398. This control is attributed to the improved halogen resistance of 3DT398 vs. BZT⁹ as well as a more reliable and safer field test for residual inhibitor that was developed for 3DT398. The improved corrosion performance and process control suggest that lower concentrations of 3DT398 may be used while maintaining target corrosion performance. Going forward, all trial sites are continuing to use 3DT398 and the dosage on these systems is currently being optimized.

CONCLUSIONS

Nalco Water's innovative yellow metal corrosion inhibitor (YMCI), 3DT398, offers effective corrosion protection while reducing the environmental impacts of cooling tower blowdown waste caused by traditional triazole-based inhibitors. As demonstrated in the trial data above, 3DT398 not only matches or exceeds the corrosion protection provided by BZT, TT, and CI-TT, but also demonstrates non-detectable impact on nitrifying biomass at the application dose. As the semiconductor industry continues to grow and evolve, adopting effective, nontriazole-based corrosion inhibitors like 3DT398 will be crucial to protect critical cooling assets while mitigating environmental impacts.

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