

# Development of new environmentally friendly O<sub>2</sub>-scavengers for Hydroquinone Replacement in Boiler Water Applications

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## Abstract

Boiler water systems as universally used throughout industry are usually protected against corrosion by addition of oxygen scavengers to the boiler feed water. Frequently used additives today are based on diethylhydroxylamine (DEHA) and its derivatives. Those formulations exhibit very good oxygen removal properties under boiler water conditions while being non-toxic.

A shortcoming of DEHA-based oxygen scavengers is the sluggish kinetics of oxygen capture in the feeding waters at low and medium temperatures. The usual remedy for this is the addition of co-scavengers, of which hydroquinone (HQ) is the most frequently used. The need for hydroquinone replacement arises from its unfavourable ecological properties, which put DEHA-HQ formulations under increasing pressure from environmental regulations.

In this work, we present an array of laboratory and application techniques suitable for the screening and identification of potential HQ replacements under a wide variety of experimental conditions. Electrochemical techniques have been developed which allow for both elucidation of reaction mechanisms and kinetics as well as fast identification of suitable substances. In combination with on-line recording of oxygen reduction kinetics this represents a set of tools suitable for both formulation development and adaptation to specific customer needs.

Two distinct substance groups (organic co-scavengers and oxidation catalysts) have been found that in conjunction with DEHA attain the performance level of DEHA-HQ with significantly less environmental impact. The new co-scavengers function as a direct replacement of hydroquinone in existing formulations, while oxidation catalysts can be used in even lower concentrations since they are not being depleted in the DEHA-O<sub>2</sub>-reaction process. Consequently, a great degree of flexibility is attained in dealing with boiler water corrosion under different operation conditions.

## Keywords

*boiler, DEHA, catalysts, development, electrochemistry*

## 1. Introduction

Achievement of the balance between state-of-the-art performance and ecological profile has become the major focus of development in water treatment chemicals in the past years. In view of ever increasing environmental awareness as evidenced in ever more restrictive environmental regulations, ecological properties of chemicals have become equally important to technical and economical ones - high performance and affordable raw material costs must be accompanied by environmental sustainability.

In industrial cooling water treatment, this has led to various innovations, especially in biodegradable scale and corrosion inhibitors [1-3]. Another important segment of industrial cooling water treatment is the de-oxygenation of feed water for boiler systems. A simplified drawing of a boiler system is depicted in Fig. 1 :

**Fig. 1 :** Schematic representation of an industrial boiler water system

Typical oxygen scavengers which have been employed include ascorbates, carbohydrazides, hydrazine, diethylhydroxylamine (DEHA), hydroquinone (HQ), sulfites, tannines and ketoximes. Of these, the combination DEHA + HQ has become a prominent system for both low (< 68 bar) and high pressure (> 68 bar) conditions [4-6].

In the pressurized part of the boiler system, conditions are generally favorable for facile oxygen removal kinetics with DEHA. However, below 50°C (feeding water conditions), the co-scavenger hydroquinone must be added in order to accelerate the deaeration to ensure that the oxygen content of the feedwater is low enough to prevent corrosion of both feedwater reservoir and boiler vessel. The dramatic performance improvement of DEHA/HQ in comparison to the sluggish DEHA at low temperatures is readily seen from fig.2, in which the oxygen content of a typical feedwater composition as measured electrochemically is plotted versus time.

The replacement of HQ by ecologically superior chemistry and the array of testing methods employed to develop this new chemistry is the topic of this work.

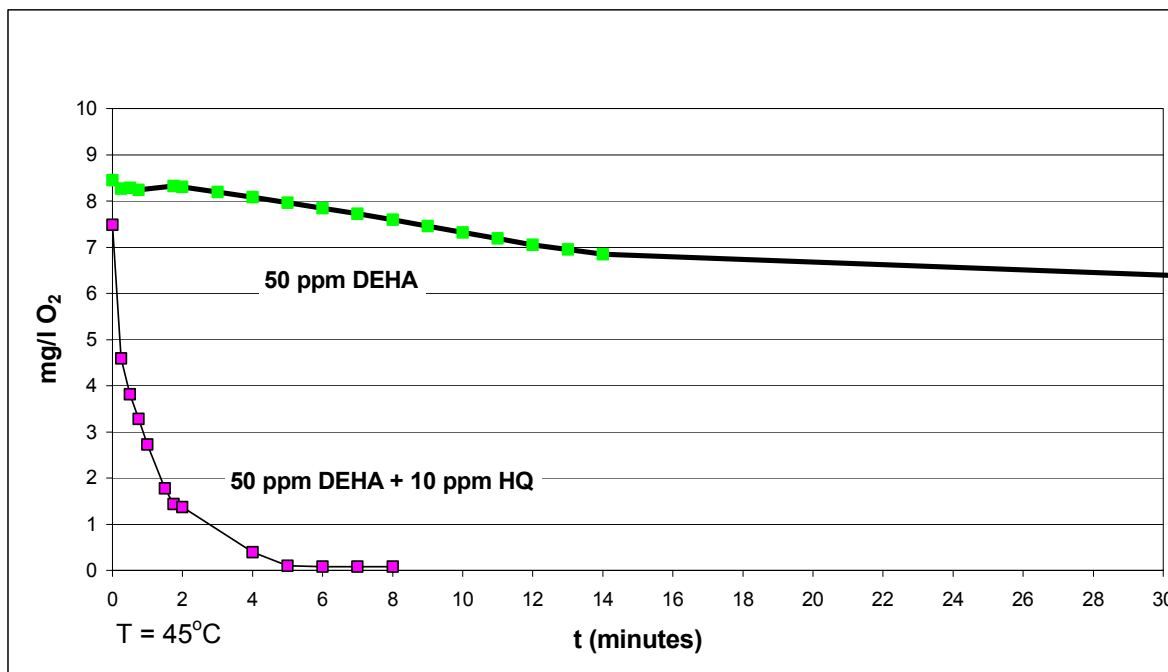


Fig. 2 : Oxygen content vs. time for pure and Hydroquinone-assisted Diethylhydroxylamine

## 2. Experimental

### *Testing Conditions*

A predefined quality of deionized water (conductivity < 1 $\mu$ S/cm) was used for all oxygen level measurements, corrosion tests were conducted in a predefined synthetic water. Inhibitor dosage for DEHA and co-scavengers was held constant at 50 and 10 ppm, respectively, for catalysts varying concentrations below 1 ppm were used. All experiments were carried out at a temperature of 45°C.

### *Electrochemical Measurements*

Electrochemical Measurements were carried out using gold electrodes in a standard three-electrode configuration with potentiostatic control. Measurement of the effectiveness for a specific oxygen remover formulation were carried out by monitoring both DEHA/co-scavenger concentrations and the O<sub>2</sub>-reduction current on Au electrodes between -0.1 and -0.4 V vs. SHE. The Oxygen content of the test solutions was also measured independently using a commercially available O<sub>2</sub>-sensitive electrode.

### *Corrosion Tests*

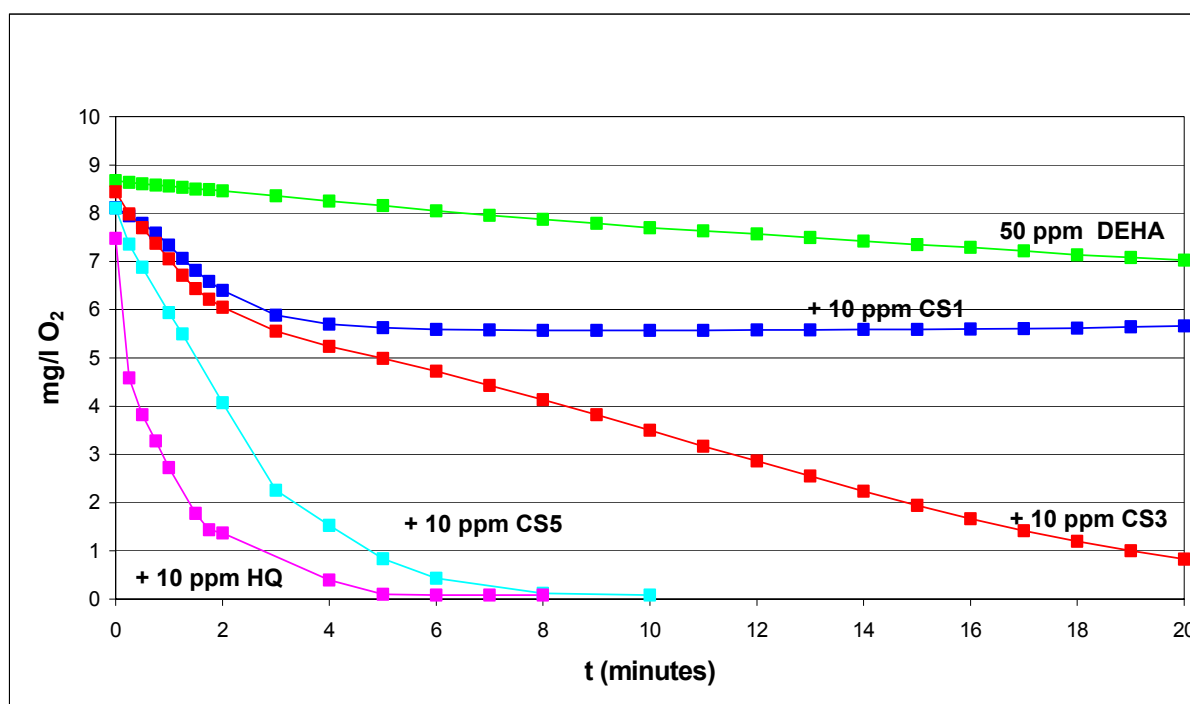
Standardized corrosion testing coupons of low-alloyed steel were used in a closed vessel. The test water containing the oxygen scavenger test formulation was then stirred for 5h. The weight loss of the coupons was then recorded as indicator for the relative corrosion rate.

## 3. Results and Discussion

### *3.1 Co-scavenger Screening : O<sub>2</sub> removal kinetics*

A two-winged strategy was employed in the search for new low-temperature boosters for DEHA. A variety of reducing agents were screened as a direct replacement for hydroquinone

("co-scavenger approach"), while at the same time a search for potential oxidation catalysts also commenced. Fig. 3 shows some representative results for the O<sub>2</sub>-removal efficiency of various new co-scavengers in comparison to pure DEHA and the DEHA/HQ-system :

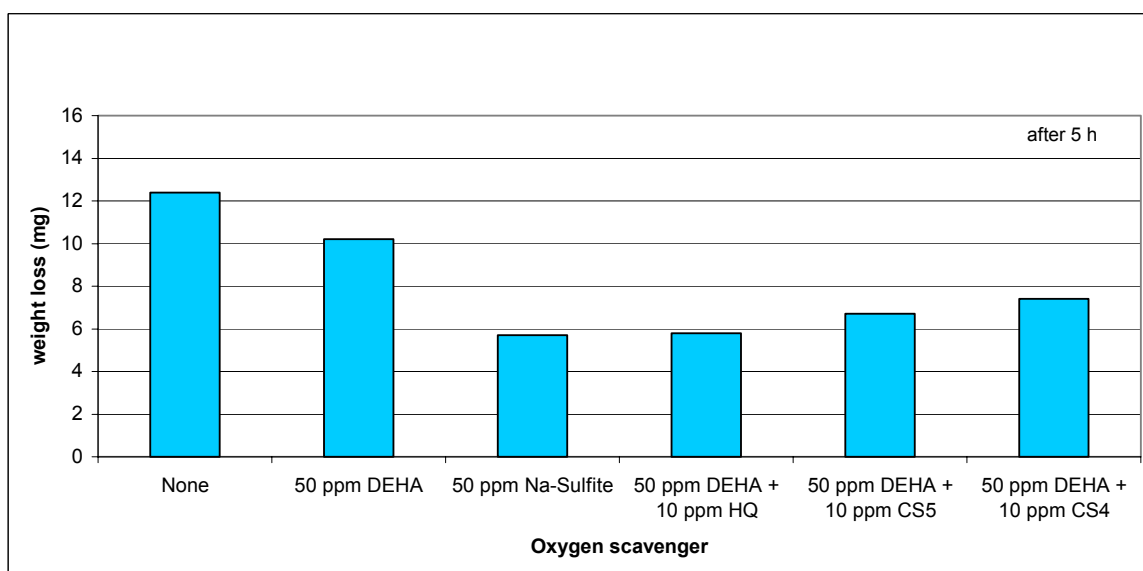
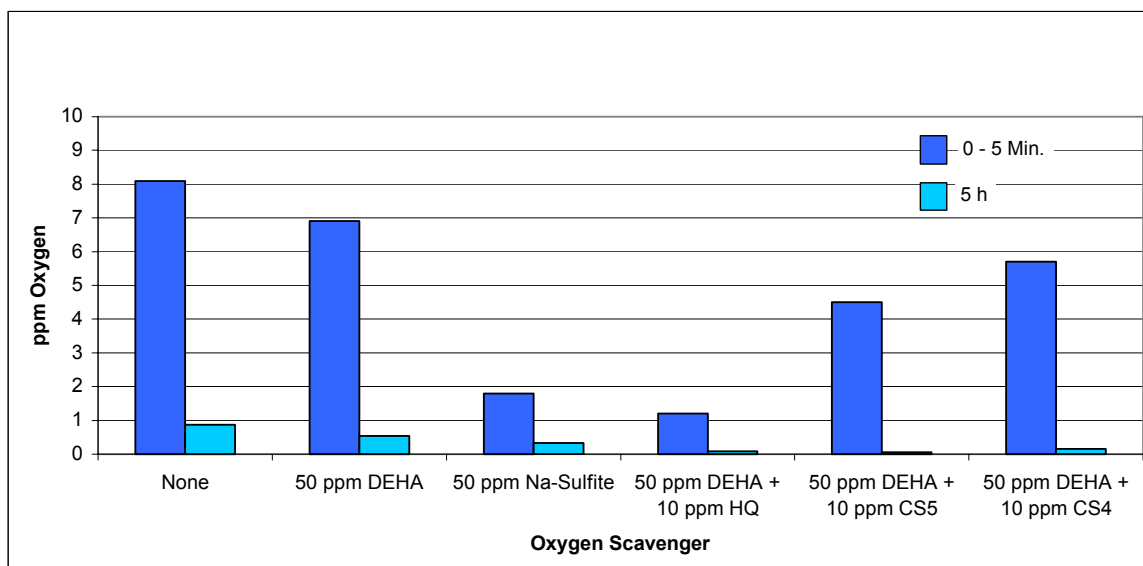


**Fig. 3 :** Oxygen content vs. time at 25°C for pure DEHA, DEHA/HQ and selected DEHA/co-scavenger (CS1-CS5) mixtures

It is easily seen from Fig. 3, that all of the added co-scavengers CS1 to CS5 significantly increase the O<sub>2</sub>-removal efficiency at 25°C when added to the basic formula of 50 ppm DEHA. The best results are obtained with co-scavenger CS5 which displays very facile reaction kinetics on the same performance level as the standard system DEHA/HQ, albeit with significantly lower environmental impact. In order to assess the further information on the impact of the new scavengers under practical conditions, additional corrosion tests were carried out with the best substances from the O<sub>2</sub>-removal test.

### 3.2. Co-scavenger screening : corrosion tests

Fig. 4a shows the absolute oxygen content of water samples with 5 different scavenger formulations after both an initial period of 5 minutes and after 5 hours (end of corrosion test). While all formulations tested exhibit a very low final oxygen content below 0.5 ppm, the initial O<sub>2</sub>-content differs significantly in correlation to the kinetics apparent from Fig.3. Fig. 4b displays the average weight loss per coupon tested in the same solutions. The suspected strong direct correlation between both initial and final O<sub>2</sub>-content and absolute corrosion rate is verified from those results. From the results shown in Fig.4b, both CS4 and CS5 appear to be promising candidates for hydroquinone replacement.

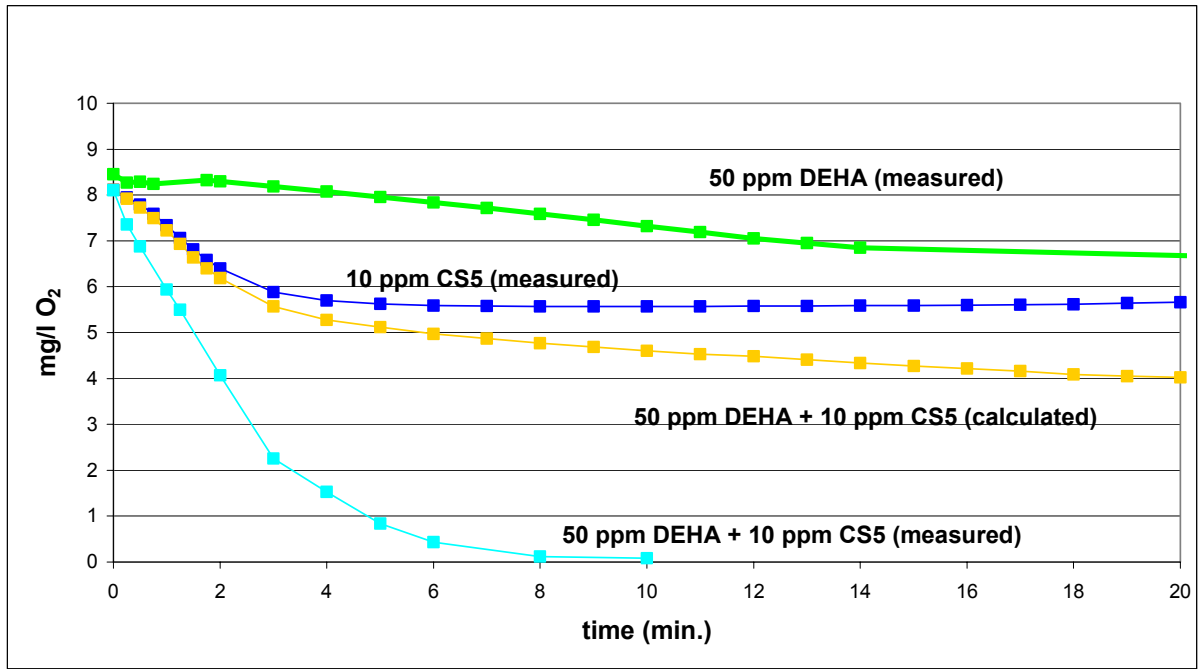


**Fig. 4a (above) :** Oxygen content of test solutions containing different O<sub>2</sub>-scavenger formulations at both start and end of corrosion testing

**Fig. 4b (below) :** Average absolute weight loss of steel coupons after 5h corrosion testing in synthetic water containing different scavenger formulations

### 3.3 Co-scavenger screening : Synergy effects

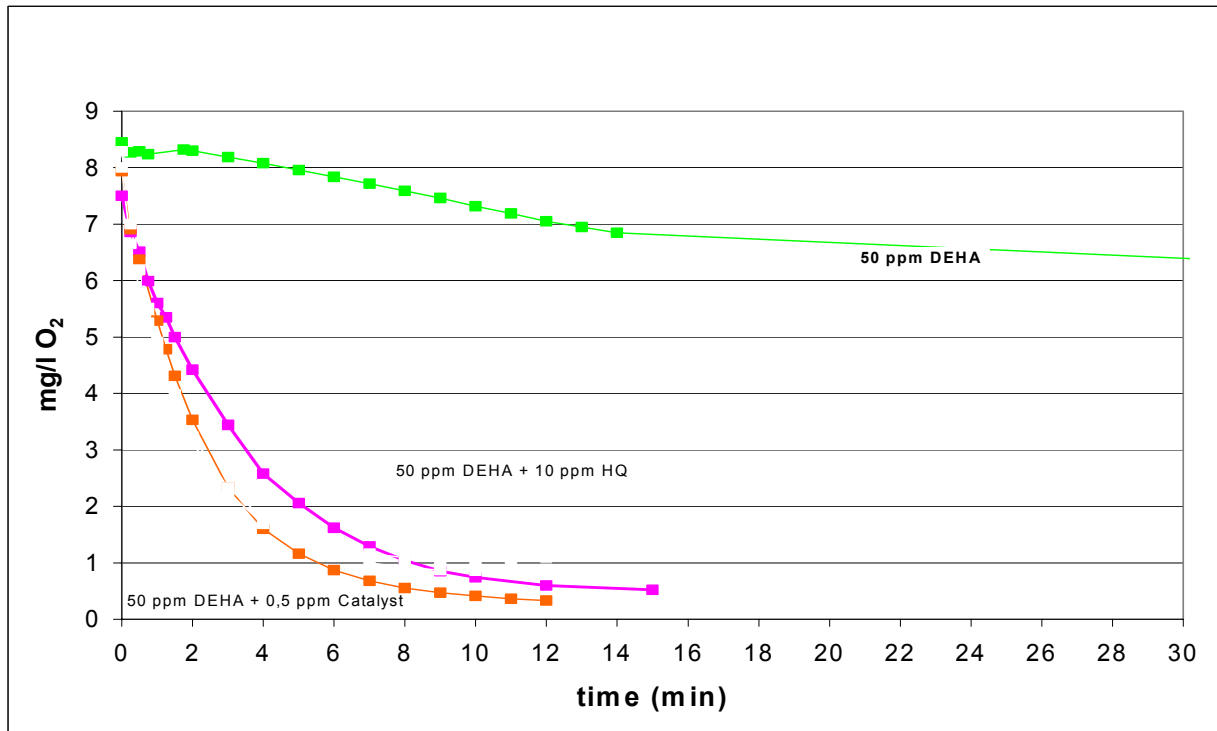
An interesting effect displayed by several of the newly discovered DEHA/CS-formulations is a pronounced synergy between DEHA and the respective co-scavenger. Fig. 5 displays a typical example of this class of effects. The experimentally measured O<sub>2</sub>-removal efficiency and its kinetics are clearly superior to the theoretically calculated summation curve obtained by adding the C(O<sub>2</sub>) = f(t) curves for DEHA and co-scavenger as measured separately. Judging from the fact that both DEHA and CS5 exhibit similar depletion rates during the experiment, this appears to be a genuine synergy effect as opposed to the catalytic interactions described in section 3.4 below.



**Fig. 5 :** Synergy effects in DEHA/CS5-mixtures. Note the much higher efficiency of the mixture in comparison to the simple addition of separated measurements

### 3.4. Catalyst screening : O<sub>2</sub> removal kinetics

Fig. 6 shows some representative results for the O<sub>2</sub>-removal efficiency of various new catalysts for DEHA in comparison to uncatalyzed DEHA and DEHA/HQ. Apparently,

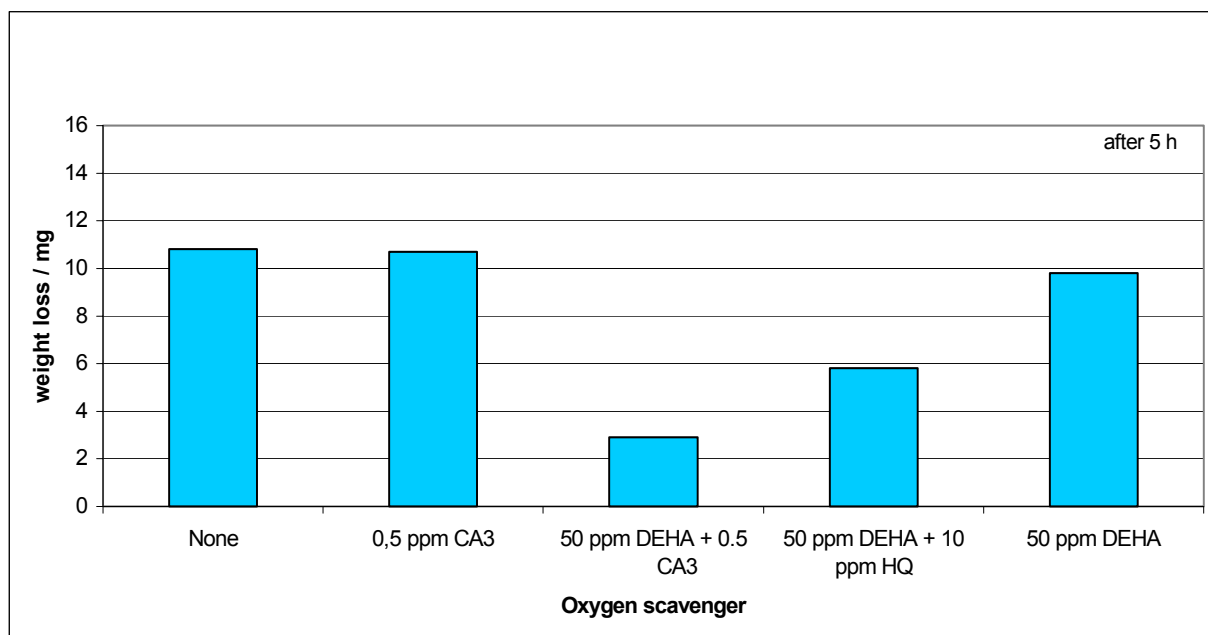


**Fig. 6 :** Oxygen content vs. time at 25°C for different DEHA/catalyst mixtures (CA1-CA7) a huge performance boost is effected by using only 0.5 ppm of active catalyst in conjunction with the basic 50 ppm DEHA. The DEHA/catalyst performance equals the DEHA/HQ

benchmark in every respect while lowering the additional chemical consumption by more than 95 %.

### 3.5. Catalyst screening : corrosion tests

This is also reflected in the results from corrosion tests as displayed in Fig. 7 with one catalyst (CA3) as an example. Clearly, the pure catalyst shows no effect by itself, but in conjunction with the basic 50 ppm of DEHA, the corrosion performance clearly exceeds the state-of-the-art benchmark set by DEHA/HQ-based formulations.



**Fig. 7 :** Average absolute weight loss of steel coupons after 5h corrosion testing in standardized water containing different scavenger formulations

## 4. Conclusions

The results shown in this work demonstrate that a replacement of environmentally hazardous components such as Hydroquinone by less dangerous ingredients is possible for oxygen scavenger formulations based on Diethylhydroxylamine (DEHA). Fast laboratory screening techniques based on electrochemical methods facilitate the screening of prospective new co-scavengers and catalysts for DEHA in such a way that both fast development of new water treatment products and rapid response to specific customer demands becomes possible.

In the case of DEHA-based O<sub>2</sub>-scavengers, two distinctively different approaches for Hydroquinone replacement can be taken :

- Being a co-scavenger itself, Hydroquinone can be replaced by less toxic substances approaching the same level of performance.
- Alternatively, catalysts can be added in sub-ppm-measures to the basic 50 ppm of DEHA-formulation, boosting the performance level to DEHA/HQ numbers while reducing the amount of additional chemicals required by more than 95%

Subsequent steps following these promising laboratory developments up to the finished product will include :

- thermal stability testing (autoclave experiments, thermogravimetry)
- detailed environmental assessment of possible decomposition products
- storage stability of concentrated formulations
- product volatility as a function of ambient pressure
- field tests

Depending on the actual field conditions, a suitable approach may be chosen individually, which retains the operational security of classical DEHA/HQ-systems while enhancing the ecological profile of the formulation, thereby continuing the trend towards ever increasing sustainability in industrial production processes.

## 5. References

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