

NEW METHOD FOR THE EVALUATION OF DISPERSING AGENTS FOR COOLING WATER SYSTEMS

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ABSTRACT

The prevention of mineral scales and sludge presents a major challenge for industrial water systems management, e.g. cooling towers, throughout a wide variety of industrial processes. Besides threshold-active substances (hardness stabilizing agents), that inhibit the formation of insoluble precipitates such as calcium carbonate from over-saturated solutions, dispersing agents are widely applied in order to prevent settling of non-dissolved matter within water bearing systems. Whereas several reliable methods are available to characterize the efficiency of hardness stabilizing agents, there is a clear demand for a simple and fast screening method to quantify the efficacy of dispersing agents under the special conditions of cooling and process water. State of the art methods are oriented mainly towards the conditions of dispersions containing high amounts of solids, e.g. up to 50 % in paints, and do not provide any useful information within the concentration range of suspended matter in cooling systems, which is 3 to 4 orders of magnitude smaller, usually below 100 mg/l.

Therefore, a new laboratory method has been developed measuring scattering of light in dependence of time in model suspensions containing different amounts of dispersing agents, that are realistic approximation of the practical conditions of cooling systems. By application of an optimized suspension preparation and installing a robot for fully automated measuring an excellent reproducibility and repeatability was achieved. The measured data are further evaluated by linearization assuming a first order kinetic of the sedimentation process. After normalizing the slopes of the regression lines to the blind value the relative dispersing efficiency is achieved, that enables the direct comparison of the efficiency of dispersant agents.

The newly developed screening method provides a fast and reliable tool for comparative assessment of dispersing agents. This is demonstrated by data derived for dispersing agents of different chemistry and different suspended solids. The results show a clear ranking of the tested dispersing agents, that is, however, also depending on the suspended material. This enables the development of new chemical formulations and the tailored adaptation of treatment programs to the customer directly translating into mutual benefits ranging from faster response times to optimized cost-effective solutions for a wide variety of dispersing tasks.

INTRODUCTION

Industrial cooling systems, particularly open recirculating cooling systems, play an important role for the efficient operation of plants within almost all kinds of industries, e.g. power plants, steel mills or even food processing plants [1]. However, cooling system management has to deal with numerous technical problems related to the usage of water: scale formation, corrosion and microbiological growth. A poor cooling system operation can have a serious impact on operational cost and environmental burden as well as on the workers' and public health. As a consequence several guidelines have been issued to describe the recommend practice of cooling system operations [2, 3].

For illustration the condenser of a main cooling system of a power plant is considered. Clean surfaces of the condenser tubes are crucial for an optimal heat transfer enabling maximum energy production. If scale formation occurs, cooling efficiency and finally energy production is reduced. A reduction of the temperature difference of only 1 °C between the water inlet and outlet in the main condenser leads to an efficiency loss of approximately 3.5 KW/MW, which corresponds to an economical loss of 2,500 €/day in case of a 1,000 MW plant [2].

Furthermore, the accumulation of sludge in the cooling systems significantly favors microbiological growth and thus significantly increases the risk of the occurrence of pathogenic species like legionella or amoebae[4, 5].

An important counter measure is the application of a cooling water treatment, i.e. the dosage of chemical additives to the cooling water. Anti-scalants used at low concentrations successfully prevent the formation of deposits and thus represent state of the art cooling water treatment. The mode of action of anti-scalants consists of two different mechanisms, that are defined in this paper as 'hardness stabilization' and 'dispersing'. Unfortunately, these terms are used within the literature in an ambiguous manner.

Hardness stabilization prevents the precipitation of insoluble salts from super-saturated solutions. The evaporation of water in cooling towers leads to an upgrading of the dissolved salts in the cooling water. As a consequence the solubility product of salts can be exceeded and, therefore, precipitation of these salts will occur. If hardness stabilizers are used the precipitation can be totally inhibited, even if the solubility products are surpassed many times. The efficiency limits of hardness stabilizers are depending on their chemical structure, the precipitate – calcium carbonate is by far the most important - and operational conditions.

Dispersing agents prevent the settling of insoluble compounds in the system. The suspended matter is kept in the fluid phase and thus is removed from the system by the normal blow-down. Insoluble matter is incorporated into cooling systems with the make-up water -often untreated surface waters used for this purpose-, by the air-washing effect of the cooling tower and finally by precipitation of salts.

As a consequence, a modern treatment program with anti-scalants should comprise both hardness-stabilising and dispersing agents. Although the phenomena are somewhat related to another, they should be considered separately in order to adapt optimally the program to the specific demands of the individual cooling system.

In order to develop tailor-made treatment programs the supplier has to evaluate additives and programs regarding their efficiency. Therefore, various test methods are used in order to simulate the conditions of a cooling system under practical oriented conditions, that differ considerably from the level of necessary effort and expressiveness of the results. Whereas on the one hand side screening methods are oriented towards high through-put and thus are limited, on the other hand side complex pilot plant studies closely simulate the conditions

of a specific cooling system. The first kind of test is applied to characterize additives under controlled conditions enabling a relative comparison, the latter ones are used for a comprehensive evaluation of treatment programs.

Whereas the layout of pilot plant cooling systems are well described [6 – 9] as well as several screening methods have been established for the evaluation of hardness stabilization [10 – 12], there is a lack of a suitable screening method for the evaluation of dispersing agents under cooling water conditions [13 – 15]. This paper presents a newly developed test method for a rapid and reliable determination of the relative dispersing efficiency of dispersing agents. It is based on spectroscopic analysis of low-solid dispersions in dependence of time. The basic approach reported in [16] has been further developed and optimized.

EXPERIMENTAL

General considerations:

A screening method has to provide reproducible results with reasonable precision under controlled test conditions that reflect a realistic worst case scenario of the practical conditions. Furthermore, a test method has to be able to run several tests in parallel and the test duration should be limited best to a working day, i.e. to app. 8 hours. Certainly, the level of sophistication should be limited to ensure that different people are able to do it.

Taking into consideration these demands, it can be noticed that the majority of screening methods are far from being suitable for the conditions in cooling water. State of the art methods often are oriented to the mineral or paint industry and thus are operating at a level of suspended matter, that is in the concentration range of percent of g/l. However, in cooling systems the concentration of suspended solids is generally below 50 mg/l (3-4 orders of magnitude lower), so that different mechanisms will be dominant for the dispersing effect.

Although the concentration of suspended matter in cooling systems is low, an efficient dispersing agent is necessary in order to keep the systems clean (which is a major strategy against legionella). A cooling system using 1,000 m³/h make-up water with a level of 20 mg/l of

suspended matter is considered. If 50 % of the suspended matter settles inside the system, the annual amount of sediment accumulated in the system sums up to 86 t, assuming 8600 hours of operation.

Those methods using reasonable amounts of suspended solids show a significant lack of reproducibility. They generally measure the extinction or light scattering after a defined period of time, which is according to our investigations subject to a considerable error.

Spectroscopic screening method:

Suspended matter: The choice of the suspended material used for the investigations appeared to be crucial for the success of the project. As the suspended matter shouldn't react with the water during the period of the test, some kind of materials couldn't be used, although they play an important role in cooling systems. Calcium carbonate, calcium sulfate as well as silicate have a solubility, that varies considerably with pH and temperature. These parameter couldn't be controlled with the required precision in a reasonable way. Experiments with kaolin showed limited reproducibility. Iron oxide represents the corrosion products and is commercially available in a standardized form. Although silicon nitride is less polar than silicon oxide, the sedimentation behavior should be similar. Furthermore, it is totally inert in water. Therefore, it was chosen as a standard material.

Sample preparation: 8 beakers containing a defined suspension are prepared by weighting the exact amount of solid (30 mg iron oxide resp. 50 mg silicon nitride) into a small beaker (25 ml). After addition of water the samples are treated with ultrasonic to ensure the complete formation of primary particles. This dispersion is transferred into the measuring beaker (1000 ml) and filled up to 500 ml with a defined test water (table 1). This suspension is again treated with ultrasonic and transferred into the automatic measuring unit. The pH of the suspension is adjusted to 8.5 ± 0.1 by addition of dilute sulfuric acid respectively potassium hydroxide. The dispersing agent is added to the suspension and the suspension is heated up to 37 °C in a thermo-stated water bath while stirring under high rotation speed (250 rpm).

Compound	Concentration [mg/l]	Concentration [ppm CaCO ₃]
Magnesium	0.6	60
Calcium	0	0
Sulfate	1.5	
Chloride	4.1	
Bicarbonate	4.4	220
pH	8.5*	
Suspended iron oxide	50	

**pH without unit*

Table 1: *Composition of iron oxide suspension for spectroscopic screening method*

Measurement: Prior to the start of the measurement the stirring speed is reduced to 35 rpm. The extinction is measured with a conventional spectrophotometer at a preset wavelength ($\lambda = 610$ nm) using a fiberoptic probe. The measuring is carried out by a automatic robot-supported unit developed especially for this application (Figure 1). The spectrophotometer probe is mounted on a vertically oriented robot arm, that is connected to a horizontally oriented one. Due to the x-y-robot the probe can be directed towards predefined positions. It sequentially measures the extinction in the beakers at a fixed filling height. The probe is automatically cleaned after each measurement. Generally, the interval between two measuring series is 10 minutes. The control of the robot and the data accumulation is carried out by an external interface connected to a computer. The control software evaluates the gained data preliminarily. The raw data can be exported in a standard format and thus are available for further data processing. Typically, the measurement period is app 6 hours.

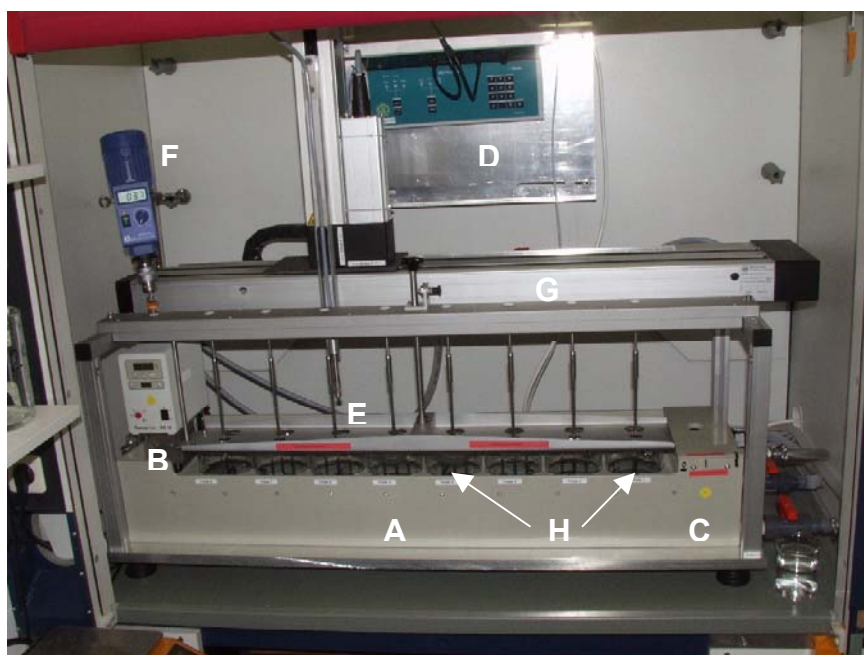


Figure 1: Picture of the automated unit for measuring the relative dispersing efficiency of additives. A) plastic water basin; B) thermostat; C) probe cleaning; D) spectrophotometer; E) fiber-optic probe; F) stirrer; G) robot arms; H) beakers. The interface and the computer are not shown.

Data evaluation: The raw data are automatically corrected by the extinction measured after the cleaning procedure. Thus, curves of the extinction in dependence of time are obtained. Figure 2 shows a typical result for iron oxide suspension and varying concentrations of a copolymer as dispersing agent. It is evident that the extinction at the beginning of the measuring period is submitted to considerable deviation although theoretically it should be the same. This can be explained that the sedimentation process already starts during the sample preparation phase. A decrease of the preparation time, however, significantly reduced the reproducibility of the measurement.

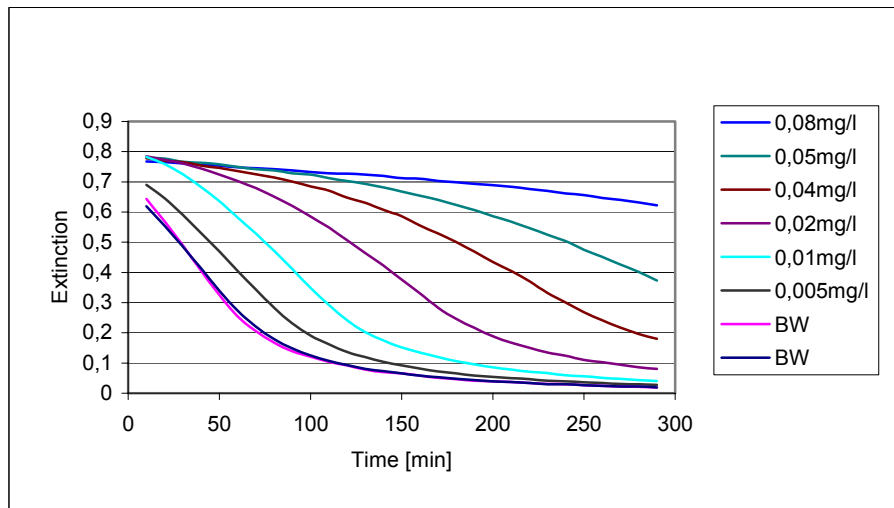


Figure 2: Extinction in dependence of time for iron oxide suspensions and concentration of dispersing agent (acrylate copolymer). $T = 37$ °C. Conc. of iron oxide = 60 mg/l.

In order to eliminate the influence of any difference in the starting extinction the data are further processed by approximation with a first order kinetic law. Thereby, the concentration gradient over time of the suspension at a certain height in the beaker can be written as:

$$\frac{\partial c}{\partial t} = -a \cdot c$$

$$\int_{c_0}^{c_t} \frac{\partial c}{c} = -a \cdot \int_{t_0}^{t} \partial t$$

$$c_t = c_0 \cdot \exp(-a(t - t_0))$$

with the boundary condition $t_0 = 0$

$$c_t = c_0 \cdot \exp(-a \cdot t)$$

is achieved. Assuming the validity of Lambert Beers law, an exponential decay of the extinction versus time is obtained:

$$E(t) = E_0 \cdot \exp(-a' \cdot t)$$

After linearization the following equation is achieved

$$\ln(E(t)/E_0) = - a' \cdot t$$

The proportional constant a' is a measure of the velocity of sedimentation and it is independent of E_0 the extinction at the start of the measurement. Figure 3 shows the plot of the natural logarithm of the extinction versus time of the data from figure 2. It can be seen that the first order kinetic approach describes the behavior of the system in a satisfying manner. The slope of the linear regression analysis is taken for further data evaluation. The lower the slope the better is the efficiency of the dispersing agent.

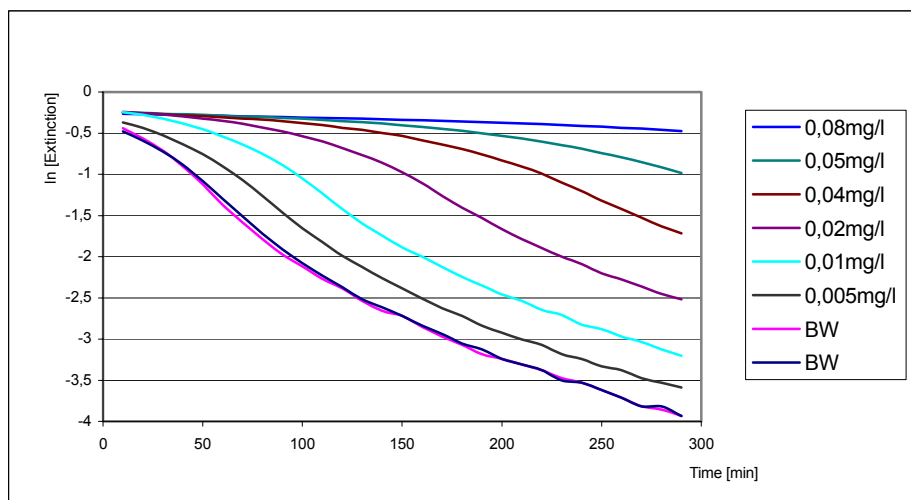


Figure 3: Natural logarithm of the extinction in dependence of time for iron oxide suspensions and concentration of dispersing agent (acrylate copolymer). $T = 37 \text{ }^\circ\text{C}$. Conc. of iron oxide = 60 mg/l.

For comparison of the efficiency of different dispersing agents the slopes are normalized against the reference value without addition to determine the Relative Dispersing Efficiency (RDE [%]). The reference value is defined to be 0%. A RDE of 100 % would correspond to horizontal line (no sedimentation at all) with a slope of zero. The RDE for a given dispersing agent concentration RDE(c) is

calculated from the slope measured for this concentration slope(c) and the slope for the reference value slope(c=0) according to

$$\text{RDE}(c) = (1 - \text{slope}(c)/\text{slope}(c=0)) \cdot 100\%.$$

The plot of the RDE against dispersant agent concentration is a more vivid visualization of the dispersing agents efficiency. It is analogous to the usual graphical display of hardness stabilization.

RESULTS AND DISCUSSION

Reproducibility

Systematic studies have been carried out to study the reproducibility of the spectroscopic method. Within the same series the standard deviation of the slopes for the reference value was app. 2 % for iron oxide resp. app 4 % for silicon nitride. The standard deviation of the slopes between different series was app. 4 % for iron oxide resp. app 10 % for silicon nitride. These data show that the newly developed spectroscopic method provide results with satisfying reproducibility.

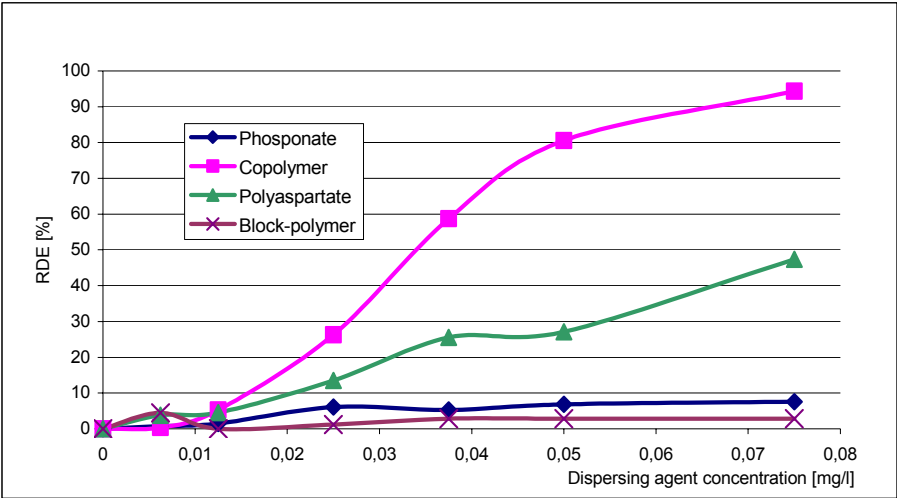
Comparison of dispersing agents

The spectroscopic method has been applied under standardized conditions for various dispersing agents. To demonstrate the ability of the method to characterize the efficiency, the results of four dispersing agents of different chemistry have been selected:

- A standard phosphonate, which is known to be an excellent calcium carbonate hardness stabilizer.
- A multipurpose copolymer based on acrylic acid
- A polyaspartate, a biodegradable scale inhibitor with good hardness stabilization properties against calcium carbonate, calcium sulfate and barium sulfate.
- A block-polymer used as bio-dispersant.

Figure 4 shows the results for the model suspension with iron oxide, figure 5 the results with a suspension of silicon nitride. It can be clearly seen that the copolymer is the most efficient in both cases followed by the polyaspartate. The block-polymer and the phosphonate, however, show almost no (iron oxide) or only poor

efficiency (silicon nitride). Very interesting is the behavior of the block-polymer, that shows a considerable dispersing efficiency at very



low concentrations, that, however, remains stable with increasing concentration of the block-polymer.

Figure 4: Relative Dispersing Efficiency (RDE) of different dispersing agents versus concentration of dispersing agent for iron oxide suspensions (60 mg/l).

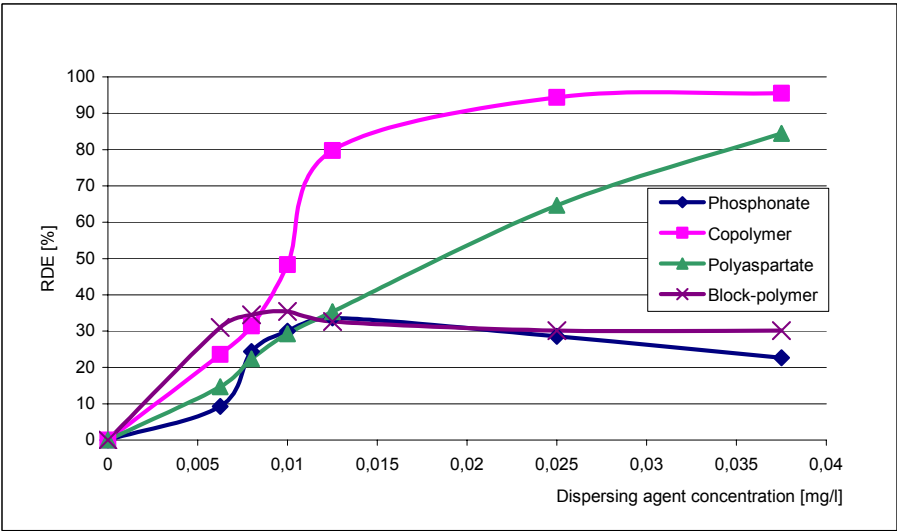


Figure 5: Relative Dispersing Efficiency (RDE) of different dispersing agents versus concentration of dispersing agent for silicon nitride suspensions (100 mg/l).

In order to understand if there might be any correlation between the hardness stabilisation and dispersing efficiency of an additive, the data of hardness stabilisation tests and biofilm removal tests have been analysed. As an example the results of a standard screening method for calcium carbonate stabilisation are shown in Figure 6. The test method is described in detail in [9].

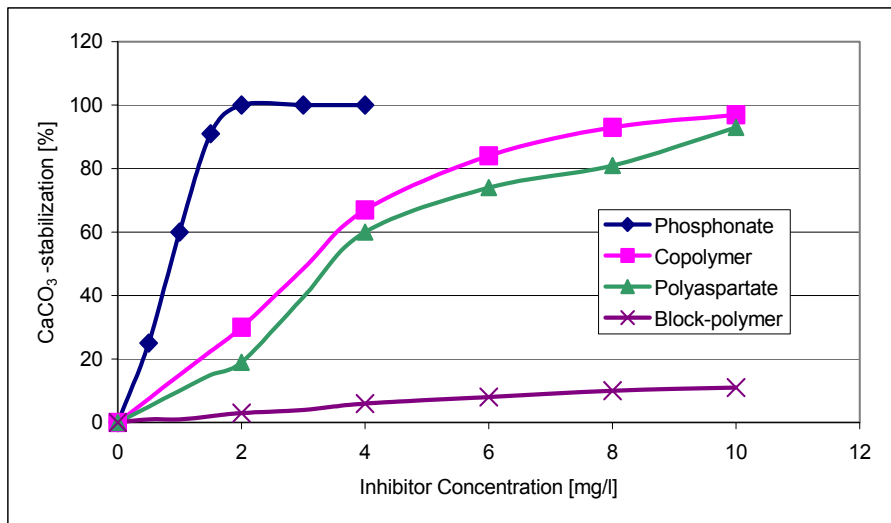


Figure 6: Calcium Carbonate Stabilisation of different hardness stabilisation agents versus concentration of the stabilisation agent.

Table 2 shows a synopsis of the available data for the four different additives. It is clearly visible that there is no significant correlation between the different properties. It can be furthermore stated that there are additives with a wide range of applicability (e.g. the copolymer or polyaspartate), whereas the phosphonate and the block-polymer show good performance for a specific application only.

Additive	Dispersing efficiency	CaCO₃ inhibition	CaSO₄ inhibition	BaSO₄ inhibition	Biofilm removal
Phosphonate	None - poor	Excellent	None	Good	None
Copolymer	Excellent	Good	Good	Not tested	None
Polyaspartate	Good	Good	Good	Good	None
Block-polymer	None - poor	None	None	None	Good

Table 2: Synopsis of efficiency classification for different additives for cooling water

As a consequence it is mandatory to characterize water treatment agents very comprehensively. It is not possible to conclude from one property to another one. Therefore, a set of reliable test methods are necessary. The newly developed spectroscopic method provides a useful and reliable tool to derive quantitative data about the efficiency of dispersing agents under specific conditions of cooling water systems.

CONCLUSIONS

The use of anti-scalants is a common tool to sustain the optimal efficiency of critical parts of cooling systems, such as condensers and heat exchangers. A state of the art anti-scaling treatment comprises not only hardness stabilizers but also dispersing agents. Traditionally there was a lack of a screening method to investigate the dispersing effect of additives under the specific conditions of cooling systems. The data had to be gained by extrapolation from method operating with extremely high solid amounts or from methods with limited expressiveness.

Therefore, an automated spectroscopic test method has been developed that overcomes these restrictions. The method determines the extinction of a suspension in dependence of time and eliminates different starting conditions by a simple evaluation process. For the

purpose of comparison the data can be displayed in an usual way. The method distinguishes itself by an excellent reproducibility. Application of the new method to different additives showed a clear differentiation in the ranking of the dispersing efficiency. However, no significant correlation could be found between the rankings of the dispersing efficiency and those concerning hardness stabilisation or biofilm removal. For a comprehensive understanding of the applicability of an additive various methods have to be applied. The new spectroscopic method provides a powerful tool to study the properties of dispersing agents for cooling water.

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