

COMPARATIVE ASSESSMENT OF DISPERSANT PROGRAMS FOR COOLING WATER

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The prevention of mineral scales and sludge presents a major challenge for cooling tower management throughout a wide variety of industrial processes. The universal application of dispersants has proven itself to be a cost-effective solution to prevent the precipitation of mineral particles contained in feeding waters for industrial cooling systems.

In this paper, an integrated approach to the development and application of new ecologically friendly dispersant systems for cooling water as an example for such processes is presented. A variety of static as well as dynamic monitoring techniques for dispersant performance is presented, ranging from fast on-site testing methods such as turbidity monitoring to sophisticated laboratory techniques such as light scattering and Zeta-potential measurements. This coherent framework of testing procedures yields comprehensive information ranging from sedimentation mechanisms to optimum concentration balances as a function of key process parameters (temperature, flow rates, water quality) under practical conditions. 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. This is demonstrated by a case study of the cooling water treatment at a nuclear power plant.

1. INTRODUCTION

Any industrial application involved with large amounts of water faces the challenge of controlling the formation of precipitates on piping systems, heat exchangers and other functional parts^{1,2}. Due to the precipitation of alkaline earth salts and silicates from untreated fresh water readily taking place on condensers, heat exchangers and piping systems, severe problems relating to operation, functionality and lifetime of mechanical equipment are encountered. This directly translates into increased costs.

Furthermore, depending on both the conditions in the flowing water system and the local conditions (e.g. amount of suspended solids, ion content, temperature, flow rate, dust), the dispersion of suspended solids becomes a major concern for the operational safety of such installations. Especially sharp changes in the suspended solid content of cooling waters due to fresh water addition have to be considered to prevent scaling and clogging of piping systems in industrial installations such as power plant cooling facilities. Since the complete removal of suspended solids from process waters is not a feasible approach if large volumes are used, dispersants are widely used for the purpose of stabilizing the particles and preventing precipitation.

Conventional screening methods for dispersants, such as the ones utilized by the manufacturers, are usually optimized for conditions of high solid content in the g/l-range^{3,4}. Those testing conditions are generally not relevant for dispersant performance assessment under cooling circuit conditions, in which much lower solid contents in the mg/l-range leads to changes in sedimentation mechanisms which can make classical methods unsuitable for the evaluation of dispersion stability.

In this paper, we present a new method of dispersant evaluation based on spectroscopic analysis of low-solid dispersions. The method is universally applicable to cooling circuit conditions and can be used both in the laboratory for screening purposes and in the field for control of treatment efficiency. Correlation of dispersant efficiency as obtained by the new method are compared to fundamental studies employing Fraunhofer diffraction and Zeta-potential measurements to demonstrate the validity of the approach.

2. EXPERIMENTAL

2.1 Agglomeration kinetics of suspended solids

The first step for the screening of new prospective dispersants is the evaluation of the agglomeration kinetics of the suspended solid particles in a defined water quality with and without the addition of active substances. In order to achieve this, 60 mg kaolin are suspended into 100 ml of standard water quality and subjected to ultrasonic mixing for 120s. The resulting dispersion is transferred to the tempered reaction vessel containing 500 ml of pure test water and stirred continuously at a defined rate of 200 r/min, thereby closely adhering to cooling water conditions with respect to the solid content. A concentration of 0.5 ppm dispersant and a monitoring time of 4 h was chosen for all experiments.

The evaluation of agglomeration kinetics is achieved by pumping the test solution through the measurement chamber of a standard Fraunhofer-Diffraction particle size apparatus (Malvern, HeNe-Laser). The particle size distribution is recorded on-line as a function of time and the time-dependence of the X_{90} -value (diameter of 90% of all particles is below this value) is then plotted to yield the absolute agglomeration curve. Comparison to the reference value without dispersant addition then yields the relative agglomeration rate which can serve as a guideline for expected dispersant performance. Besides its ease of use and fast data acquisition characteristics, this method offers the advantage of providing objective physical parameters to be correlated to application tests.

2.2 Dispersion stability: Zeta potential measurements

The stability of the dispersions is practically evidenced by the agglomeration rate and subsequently the sedimentation of the agglomerated particles, which on the laboratory scale correlates to the measured Zeta-potential, with higher Zeta potentials corresponding to more stable dispersions. In general, Zeta-potentials above 40 mV correspond to good dispersion stability, excellent stability is indicated by Zeta-potentials above 50 mV. Consequently, Zeta-potential measurements were carried out to validate the sedimentation rate results from the new spectroscopic screening method.

Experiments were done on two different idealized solid systems resembling different cases of practical relevance (iron oxide and kaolin), using a standard Zeta-potential apparatus (Malvern Zetasizer). Test systems used were prepared in standardized water by addition of

60 mg/l iron oxide or 200 mg kaolin, respectively. Experiments were run in dependence on dispersant concentration from 0 to 0.08 mg/l. Computerized evaluation of the data then yields the Zeta-Potential. The measured Zeta-potential is then correlated to the relative dispersing efficiency (as measured by the spectroscopic method described below in 2.3), therefore enabling the verification or falsification of the method used for sedimentation rate measurement.

2.3 Dispersion stability: New spectroscopic screening method

Sample preparation. 300 ml of test water are mixed with 400 mg of the solid to be tested (kaolin or iron oxide) and the total volume is then filled to 2000 ml. The suspension is homogenized by stirring and then treated ultrasonically to ensure the formation of primary particles. The dispersion is then distributed into identical vessels, stirred at high rotation speed for 15 minutes and then continuously stirred at low rotation speeds under controlled temperature conditions. The pH is adjusted to 8,5 using dilute H₂SO₄ and KOH, respectively.

Measurement. 10ml-samples are taken from the bulk of the solution, filled into a spectrometric quartz cuvette and homogenized ultrasonically for 2 minutes. The extinction is then measured with a conventional spectrophotometer at a wavelength of $\lambda=490$ nm. Since the absolute extinction values can vary considerably depending on the starting conditions, the natural logarithm of the extinction is recorded as a function of time. The resulting graphs show a very good linearity and small deviations regardless of the starting conditions. The slope of the resulting linear regressions is then taken as a measure of the sedimentation rate. After normalization against the reference value without dispersant addition (=0%), the relative dispersing efficiency can be determined. This procedure ensures that reproducible and comparable results are obtained which are largely independent of starting conditions, albeit providing excellent sensitivity for the low solid content relevant to cooling water investigations.

These methods have the advantage of being fast and yielding a characterization of the overall stability behavior of the dispersions formed under both static and dynamic conditions. Specific agglomeration kinetics information as obtained from Fraunhofer diffraction measurements and separation characteristics are determined in dependence on substance type and amount, flow conditions, pH, Temperature, solution composition and suspended solid type. The spectrum of laboratory methods can be used for both characterization and fast initial screening of new prospective dispersants as well as fine-tuning of complete formulations to specific application environments, thereby providing an efficient pathway towards specific customer-tailored solutions.

3. RESULTS AND DISCUSSION

3.1 Agglomeration kinetics

Fig 1 displays the X₉₀-values of suspended kaolin particles as a function of time for several dispersant systems.

The untreated system clearly shows the expected fast aggregation of the primary particles ultimately leading to complete separation of the system. Of the dispersants shown in Fig.1, the system based on the copolymer clearly shows the best performance yielding nearly zero agglomeration change within the time observed. A slight increase in agglomeration is observed for the acrylate-based system. It can therefore be expected that the copolymer will outperform the polyacrylate with respect to its dispersing abilities under cooling circuit conditions.

3.3 Dispersion stability: Zeta potential measurements

Fig. 2 shows the measured Zeta potentials for kaolin particles as a function of dispersant concentration from 0 to 0.08 ppm for both the acrylate and the copolymer-based system.

Clearly, both systems show a comparable stability for the kaolin dispersion, with the copolymer slightly outperforming the polyacrylate at higher concentrations. The measured differences correspond to the trend developed by the agglomeration kinetics measurements with less sharp distinction. In Fig. 3, the corresponding results for the dispersion of iron oxide are plotted.

The generally higher Zeta-potentials of the kaolin suspension as compared to the iron oxide indicate that the former should yield more stable dispersions under the test conditions.

3.3. New spectroscopic screening method

Screening results with variable concentration. Figs. 4 and 5 show the relative dispersing efficiency for different concentrations from 0 to 0.08 ppm for both the polyacrylate and the copolymer. Clearly, both dispersants show a strong dispersing efficiency increasing with concentration. The copolymer exhibits a more pronounced increase in the relative dispersing efficiency for both types of suspended solid material. This correlates to the results obtained from Zeta-potential measurements and Fraunhofer diffraction, showing high performance for both systems with the copolymer still outperforming the polyacrylate-based system.

Fig. 6 shows the complete correlation diagram for the dispersants for two different kinds of suspended solids. The diagram indicates a good correlation between the experimental results from the Zeta-potential measurements and the spectroscopic screening method.

The spectroscopic screening method has thus been validated by two different independently carried out measurements. Its accuracy and sensitivity combined with ease of use and the option to be implemented as an on-site monitoring tool clearly pose a significant improvement towards both enhanced control and monitoring of dispersant performance in cooling circuits and the fast laboratory scale evaluation of critical conditions or new formulations.

4. CASE STUDY

Cooling Circuit at a Power Plant

At a European nuclear power plant with an electrical capacity of app. 1000 MW cooling the main condenser is achieved by an open recirculating circuit. Condenser tubes are made from stainless steel and water chambers are protected by a special coating. Sponge ball cleaning with rubber balls is used to keep tube surfaces mechanically clean. The temperature difference of the water between condenser inlet and condenser outlet is app. 14

°C (32 °F) and the maximum water temperature is 40 °C (104 °F). The size of the cooling system is 20,000 m³. Water losses by blow-down and evaporation are compensated by river water, which is softened with lime and filtered through sand filters. Flocculation aids are used to optimize settling of solids in the lime softening unit. Table 1 shows a typical analysis of the make-up water :

Table 1: Typical make-up water analysis of open cooling system

pH	9.3		
Conductivity	188 $\mu\text{S/cm}$	18.8	mS/m
Total Hardness	0.9 mol/m ³	90	ppm CaCO ₃
Calcium	0.7 mol/m ³	70	ppm CaCO ₃
Total Alkalinity	0.4 mol/m ³	20	ppm CaCO ₃
Chloride	0.4 mol/m ³	14.2	ppm
Phosphate	< 1 mmol/m ³	< 0.1	ppm
Silicate	25.2 mmol/m ³	1.5	ppm
Sulfate	0.42 mol/m ³	40,4	ppm
Suspended Solids ¹⁾	14.0 g/m ³	14.0	ppm

¹⁾ by filtration through membrane filter (pore size: 8 μm)

The main cooling system is operated at a medium cycle of concentration of 6 determined by the chloride level. Blow-down is controlled by a pre-set level of cooling water conductivity. The cooling water contains a considerably high amount of suspended matter. The concentration of suspended solids is generally between 15 and 25 ppm but can increase up to 50 ppm. Table 2 shows a typical analysis of the cooling water.

Table 2 : Typical cooling water analysis of open cooling system

pH	8.1		
Conductivity	1,044	$\mu\text{S/cm}$	104.4 mS/m
Total Hardness	4.8	mol/m ³	480 ppm CaCO ₃
Calcium	3.6	mol/m ³	360 ppm CaCO ₃
Total Alkalinity	1.1	mol/m ³	55 ppm CaCO ₃
Chloride	2.3	mol/m ³	81,7 ppm
Phosphate	< 1	mmol/m ³	< 0.1 ppm
Silicate	137.8	mmol/m ³	8.3 ppm
Sulfate	3.25	mol/m ³	312 ppm
Suspended Solids ¹⁾	22.2	g/m ³	22.2 ppm

¹⁾ by filtration through membrane filter (pore size: 8 μm)

Traditionally, the cooling water had been treated by a conventional hardness stabilizer. Inspection of the condenser during regular maintenance shut-down period showed satisfying results of cooling water treatment.

To optimize the treatment efficiency the Henkel water treatment specialists made a detailed assessment of the plant and water conditions. The water data indicate that the tendency of the cooling water for precipitation of calcium carbonate is moderate, i.e. the Langelier index is app 0.6. The high cycles of concentration and comparatively high level of suspended matter in the cooling water demand a good dispersing effect of the treatment rather than superior inhibition of calcium carbonate. Upset conditions, like sharp increase of suspended solids in the system may not have any impact on process safety. Furthermore, due to the location of the power plant there was a strict requirement for a phosphorous-free and environmentally compatible treatment program.

Investigations on dispersing efficiency and calcium carbonate inhibition under the specific condition of cooling systems finally led to the development of a new treatment program tailor-made to the specific requirements of this power plant. P3-ferrofos 8461 is an anionic dispersant for mineral sludge in cooling water and process water systems. It is recommended to prevent the sedimentation of suspended solids in cooling systems and heat exchangers. The product can slowly dissolve sludge deposits and remove them from the system by normal blow down. It is a liquid product based on special low molecular weight polyelectrolytes. It is non-toxic and free of phosphorous.

Within a one year period the treatment concept was evaluated in the main cooling system. Starting with a dosage of 2 ppm into the make-up water, the product was stepwise reduced to finally 1.2 ppm within the first 6 months. The dosage of 1.2 ppm to the make-up water was continued for the second half of the year. Addition of the polyelectrolyte dispersant was proportional to the amount of make-up water. During the whole period, success of the treatment was monitored by measurement of heat exchanger efficiency and visual inspection of the cooling system. Furthermore, all relevant water data were measured daily. Figures 7 and 8 show as an example conductivity and calcium level in the re-circulating cooling water for a representative period.

After one year the condenser was opened during the regular maintenance shut-down and inspected together with the power plant operators. The tubes were totally free of hard scale (Figure 9). Furthermore, there was no scale in water chambers. Figure 10 shows the excellent appearance of the cooling tower after the treatment period. It was therefore concluded, that the treatment with the dispersant combined high economic and technical efficiency with a minimum impact on the environment.

5. REFERENCES

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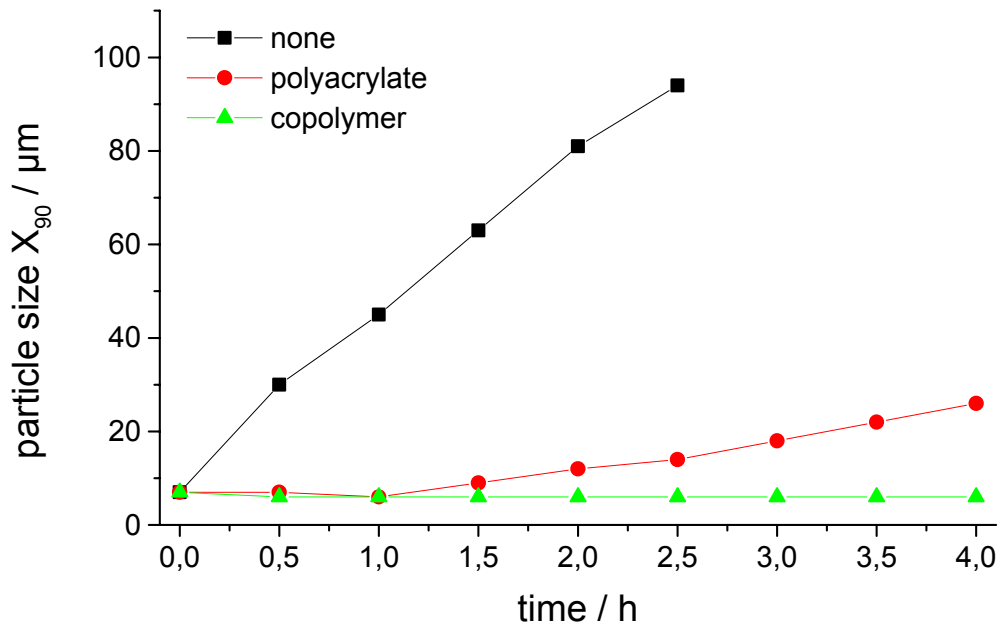


Fig. 1: Agglomeration curves of kaolin particles with two different dispersants as measured by Fraunhofer diffraction. The copolymer based formulation exhibits no discernible agglomeration over the whole time period.

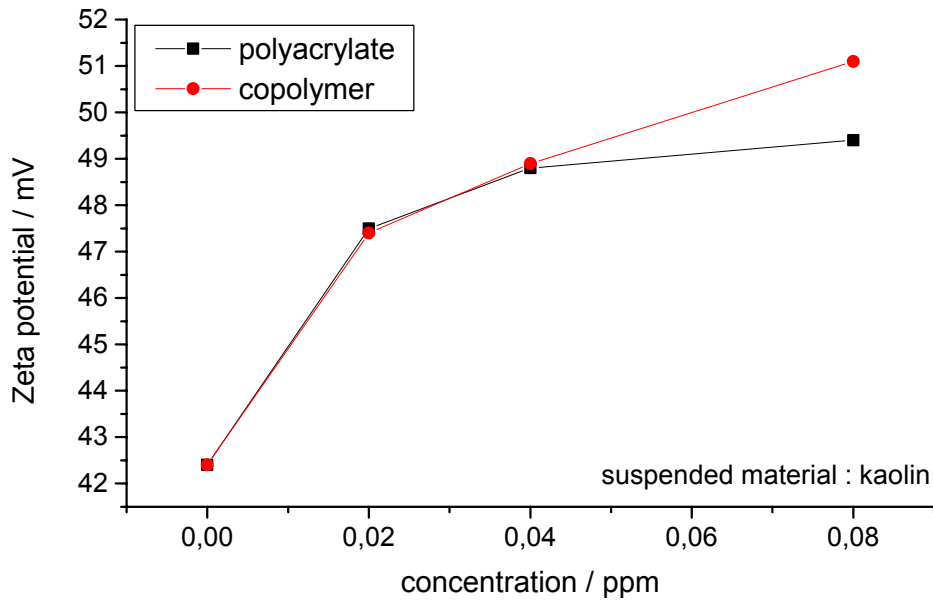


Fig. 2: Zeta potential vs. dispersant concentration for kaolin dispersions. Both formulations show a very good stabilization with the copolymer slightly outperforming the polyacrylate.

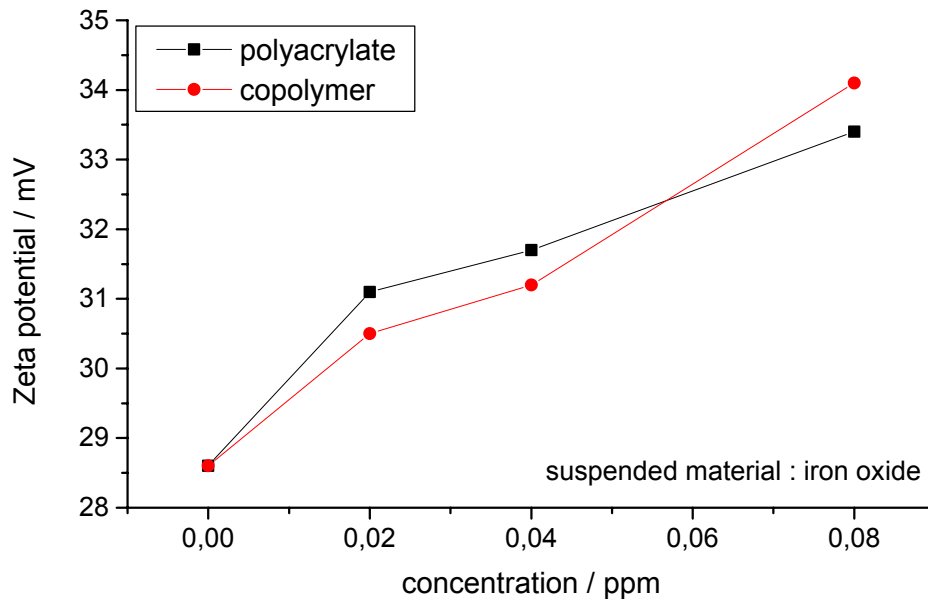


Fig. 3: Zeta potential vs. dispersant concentration for iron oxide dispersions. Both formulations exhibit very similar characteristics.

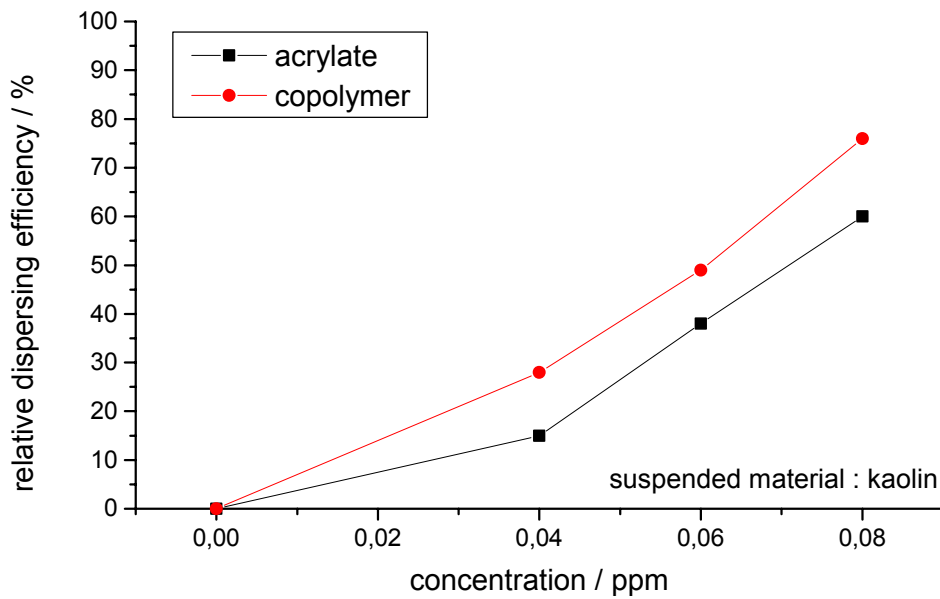


Fig. 4: Relative dispersing efficiency vs. dispersant concentration for kaolin dispersions as measured by the spectroscopic method. The copolymer shows the better performance over the entire concentration range.

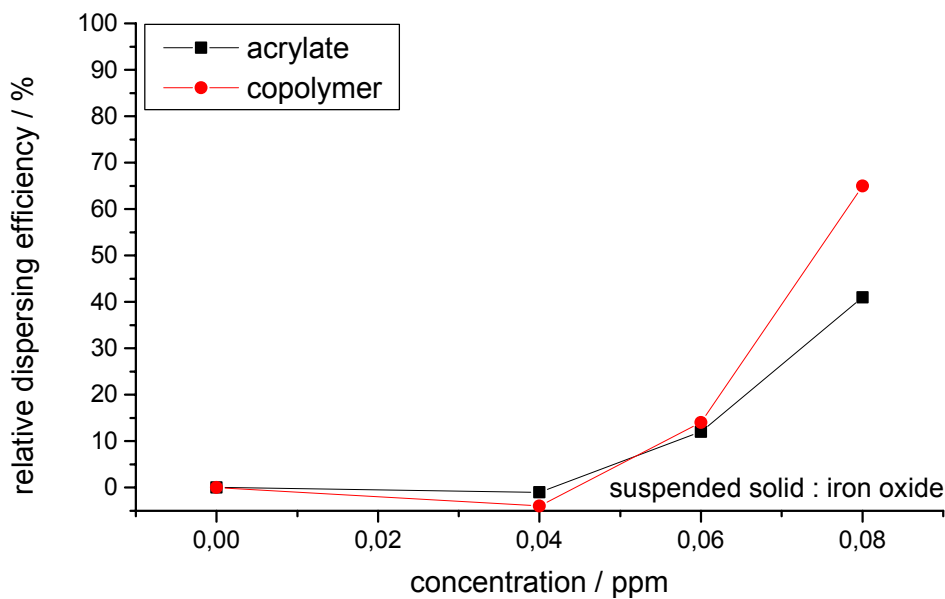


Fig. 5 : Relative dispersing efficiency vs. dispersant concentration for iron oxide dispersions as measured by the spectroscopic method. The copolymer shows the best peak performance.

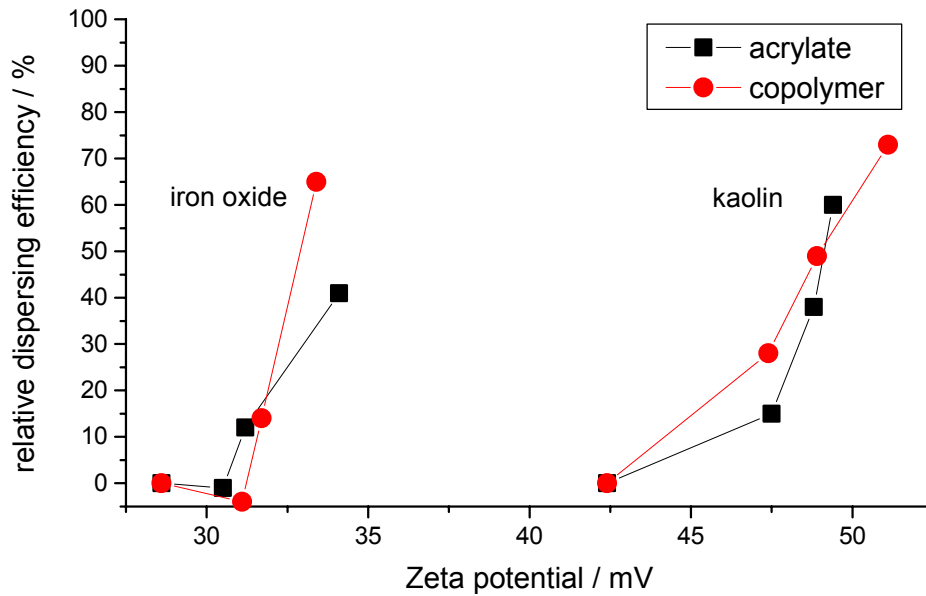


Fig. 6: Correlation diagram of relative sedimentation rate as obtained from the spectroscopic screening method with the Zeta potential measurements. Note that the sedimentation rates are comparable irrespective of solid type whereas the absolute Zeta potential values do not provide a direct comparison for different experimental conditions

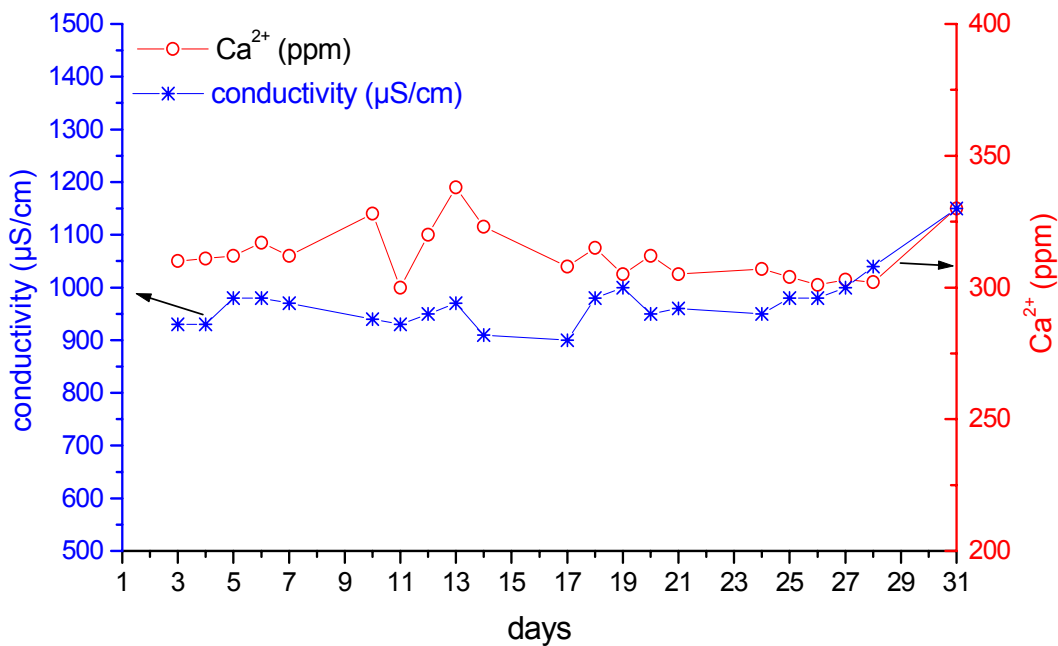


Fig. 7 : Conductivity and Calcium content of the make-up water at the power plant cooling circuit described in the Field study.

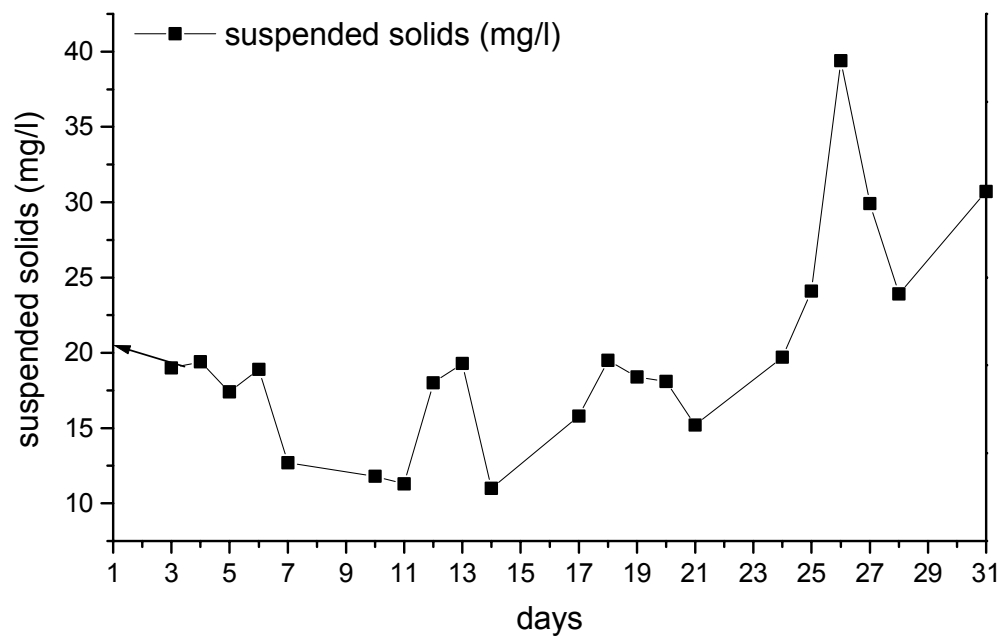


Fig. 8 : Suspended solids content of the make-up water at the power plant cooling circuit described in the Field study.

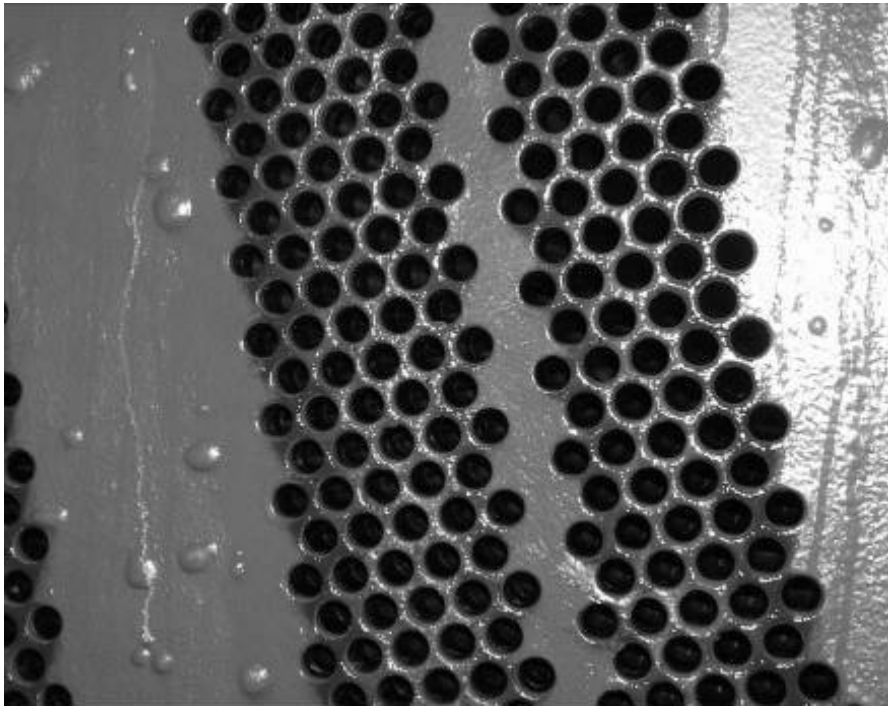


Fig. 9 : Condenser tubes in the power plant circuit after one year of continuous treatment. No visible scaling has occurred.



Fig. 10 : Overall appearance of cooling tower installations after one year of continuous treatment.