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Pilot plant experiments and modeling of CaCO_3 growth inhibition by the use of antiscalant polymers in recirculating cooling circuits

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Abstract

Recirculating cooling circuits are prone to the deposition of scale on heat exchangers and packing surfaces. The addition of antiscalant polymers is efficient for inhibiting the precipitation of calcium carbonate (CaCO_3) because polymers block the active growth sites. In this study, growth inhibition of calcite by using such polymers in industrial pilot plants operating with natural river water, which is critical to mimic a full-scale cooling circuit and accurately evaluate scale inhibition, was reported. Efficiencies of three commercial polymers were compared. The polymers thus investigated demonstrated comparable efficiencies and similar responses to changes in operating conditions.

An adsorption-based model was proposed to quantify the inhibition of precipitation kinetics with respect to the process operating conditions and water qualities. Then, the model was validated at a wide range of polymer concentrations, temperatures, and water qualities, representative of industrial systems. A small amount of polymer was sufficient to affect bulk-scale prevention, albeit the efficiency became constant at high polymer concentrations. Under these conditions, a complementary treatment such as acid injection is necessary.

Keywords: Cooling water, Precipitation, Antiscalant, Inhibition, Adsorption, Polymer

1. Introduction

Precipitation of CaCO_3 is a constraining issue in industrial operations, particularly in energy-intensive industries such as cooling circuits of thermal and nuclear power plants (Liu et al., 2012a; Rahmani et al., 2015), as well as separation processes such as distillation (Al-Rawajfeh, 2008; Ghani and Al-Deffeeri, 2010), membrane desalination and reverse osmosis (Phuntsho et al., 2014; Greenlee et al., 2010). In these processes, the precipitation of calcium carbonate occurs by the increase in water temperature and/or salt concentration, attributed to the removal of water from the liquid phase by evaporation or permeation. Hence, CaCO_3 precipitates on surfaces, and thermal or separation efficiency decreases, resulting in increased operative costs for the prevention or control of scaling. In addition, structures are weakened, requiring considerable maintenance, thereby decreasing the equipment lifespan. Among several possible treatments, the addition of soluble polymers (such as antiscalant polymer or ASP) in water is an economic way for controlling the formation of scale as they significantly decrease the precipitation of CaCO_3 at low polymer concentration, typically less than 10 ppm of active matter. A wide range of chemical compounds can be utilized, such as polymers based on acrylates, amines, phosphonates, sulfonates, and aspartates (Lin and Singer, 2005; Hasson et al., 2011; MacAdam and Parsons, 2004). As some chemicals alter the environment, e.g., phosphorous compounds, recent studies have reported the development of environment-friendly inhibitors (Hasson et al., 2011; Chaussemier et al., 2015).

Several studies have been reported either on the efficiency comparison of antiscalants between several polymers or identification of mechanisms (MacAdam and Parsons, 2004; Liu, 2011; Tang et al., 2008; Amjad, 1996; Li, 2010); however, relatively few studies have been reported on the modeling of inhibition efficiency. Two general inhibition models have been reported in literature according to the inhibition mechanism: nucleation inhibition and growth inhibition. Nucleation inhibition is used so that the induction time (period before the appearance of the first crystalline germ) becomes higher than the process residence time so as to ensure that no scaling occurs in the process. Most previous studies have proposed dose calculations based on this mechanism,

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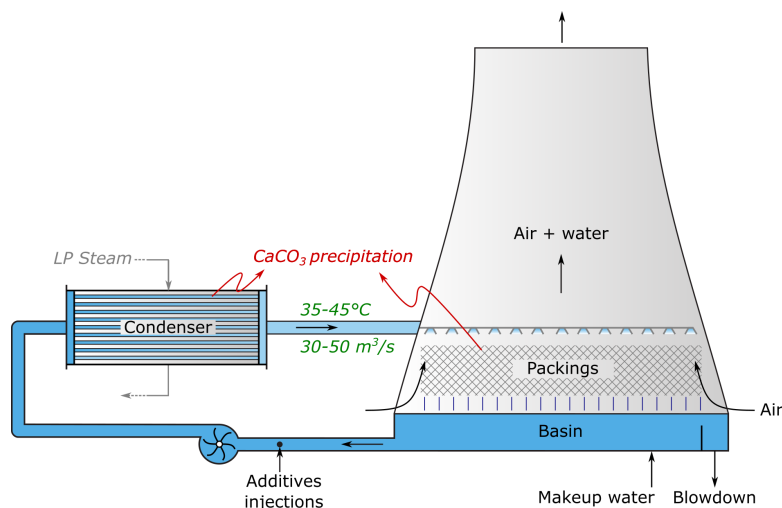


Figure 1: Wet recirculating cooling water system in a power plant

i.e., the minimum dose required for preventing germ formation. For example, experience-based orders of magnitude of inhibitor dosages have been suggested by Puckorius (reported by Cavano, 2005) with respect to the Langelier, Ryznar, and Puckorius saturation indexes for three inhibitors. He et al. (1999; 2002) have proposed a model based on nucleation inhibition by measuring the deviations with respect to induction time, linking the variation of surface energies to the inhibitor concentration; they have utilized their model for calculating the inhibitor dose required for injection with respect to the saturation index, temperature, and desired elongated induction time. Fergusson et al. (2011) has proposed a similar model for calculating the induction time with respect to inhibitor dose for several crystals such as calcite, gypsum, or barite. Vanderpool (2006) has also proposed a procedure for calculating the minimum dose required for several inhibitors, including a dose for the inhibition of homogeneous nucleation, a dose for dispersed matter, and a dose for maintaining equilibrium. On the other hand, some studies have proposed models for describing the kinetic growth inhibitor by polymers, for systems where nucleation has already occurred; hence, polymers are used for decreasing the precipitation kinetics of CaCO_3 , instead of preventing nucleation. Such models typically consider the adsorption of polymers on crystallization growth sites, with the use of adsorption isotherms such as the Langmuir, Freundlich, or Langmuir–Freundlich (Reddy and Nancollas, 1973; Kubota and Mullin, 1995; Kan et al., 2005; Lisitsin et al., 2009). The use of either a nucleation inhibition or a crystal growth inhibition model will depend on the system under study. For processes with a low residence time, such as one-through continuous flow (e.g., reverse osmosis and open cooling circuit), the inhibition of nucleation is efficient for preventing scaling. For this purpose, small quantities of polymers are sufficient to make the induction time higher than the residence time. However, for processes with higher residence times, such as in recirculating wet cooling circuits, the pragmatic viewpoint is that nucleation will occur at some point. Hence, the formation of scale is not limited by nucleation kinetics, but by crystal growth kinetics; hence, a crystal growth inhibition model is required.

In this study, emphasis is placed on recirculating cooling water systems, as shown in Figure 1, although the results obtained herein can be applied to other systems with similar operating conditions, especially with respect to water quality, temperature range, and polymer concentration. In wet recirculating cooling circuits, water is heated in an exchanger called condenser, which is then cooled in a cooling tower predominantly by evaporation, and a large amount of water is then recycled (around 10–50 times the make-up flow rate) to the condenser after cooling. Typically, for a power plant, up to several hundreds of metric tons of CaCO_3 deposits are observed annually, corresponding to a significant economic impact (Walker et al., 2012). Owing to the large volume of water in the circuit (implying a water mean residence time of several hours) and a high recirculation ratio, a large amount of chemicals are required to avoid nucleation, such as polymers to extend the induction time and/or acids to decrease the pH of water. However, this would lead to unacceptably high treatment costs and environmental impact, and hence, it cannot be performed. As a result, nucleation eventually occurs during process operation, even for initially cleaned systems; hence, polymers are added for limiting the growth kinetic rate. On the other hand, the models proposed for the inhibition of growth by polymers, such as the one reported by Lisitsin et al. (2009), are unfortunately not directly compatible with such industrial applications as they have been developed for a limited number of inhibitors, including highly legislated ones (e.g., phosphate-

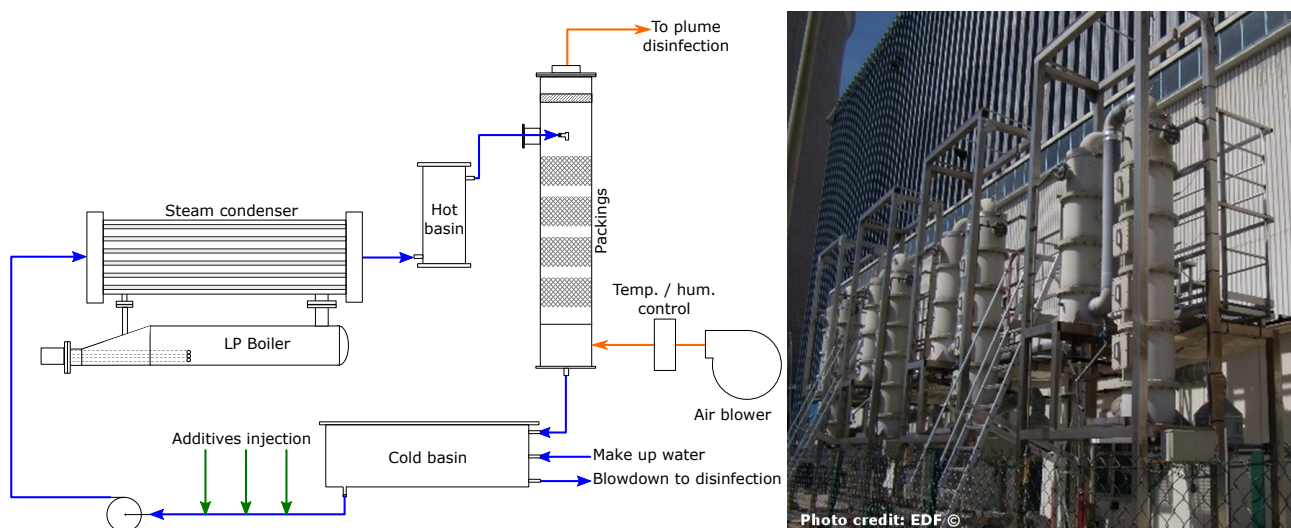


Figure 2: Schematic of a pilot plant (left) and photograph of the cooling tower skirts in Nogent-sur-Seine (right)

based inhibitors). Such models are applicable to laboratory-scale setup using synthetic waters to mimic natural raw water; and these modeling approaches are not yet validated, to the best of our knowledge, on a larger scale with natural raw water. Notably, experimental measurements have been performed in recirculating cooling pilot plants (Chien et al., 2012) using polymaleic acid (PMA), but the makeup water utilized originates from secondary-treated (Li et al., 2011) and tertiary-treated (Liu et al., 2012b) municipal wastewater and not river water, and no growth inhibition model has been proposed.

Hence, this study aims to fill the void with respect to the lack of models developed using natural water as the cooling fluid, validated for pilot-plant-scale systems. First, experiments are conducted in industrial pilot plants located in a nuclear power plant using raw river water for evaluating the efficiency of model polymers. Second, a model is proposed on the basis of the state-of-the-art models and experiments from previous studies. Finally, system-scale efficiency and model limitations, as well as perspectives for further development, are discussed.

Model development will assist researchers and engineers in designing water treatments and defining scale control strategies, focusing on the evaluation of ASP efficiency on a system scale for processes with high residence time, such as wet recirculating cooling circuits.

2. Experimental methods

2.1. Industrial pilot plant description

In this study, experimental setup is composed of four identical pilot plants, as shown in Figure 2, located in the Nogent-sur-Seine nuclear power plant (in France) owned and operated by the EDF (Électricité de France) company. Each pilot plant is mainly composed of a low-pressure steam condenser (with heat duty up to 24 kW_{th}), a counter-current cooling tower, an ambient air fan equipped with humidity and temperature control, a washing tower, hot and cold basins, a recirculation pump, and injections pumps for various additives (e.g., acids, polymers, and biocides).

The pilot plant is designed to be representative of hydrodynamics and the water chemistry as makeup water is drawn off from the power plant. The residence time in each compartment is equal to the power plant values, and the pilot plant can run utilizing the same operating conditions as those for the power plant cooling circuit. The setup is also representative of materials in the main active components as the same metals are used in the condenser tube (e.g., stainless steel, brass, or titanium) and for the cooling tower packing (e.g., structured fills); ducts, and basins are nonetheless made of plastic instead of concrete. These pilot-plant units have been operated since 2001 in several EDF facilities for studies on fouling and biological growth, as well as for the development of associated treatments.

2.2. Pilot plant monitoring

Most of the operating parameters like the cooling water flowrate, the outlet condenser temperature, the cooling tower temperature approach, the makeup water flowrate, the concentration and flowrates of each additives



are fixed by the operator. Optionally, the inlet air humidity and temperature can be fixed as well if necessary. The makeup water originating from the river, the water quality is not controlled and vary over time. In order to achieve the operating parameters targets, the air flow rate is controlled as well as the condenser heat duty and the blowdown water flowrate.

Since the purpose of this study is to evaluate the antiscaling effect of polymers, the emphasis is put on how much calcium carbonate precipitates over time. In order to evaluate the precipitation rate, one could for example measure the deposit mass on specimens but specimen only represent scaling where they are installed. A more systemic indicator is the “water calcium loss” (ΔCa), which is basically a simple mass balance in steady-state conditions between the calcium in the makeup water and that in the blowdown water. It can be expressed as:

$$\begin{aligned}\Delta\text{Ca}_{[\text{mg/L as CaCO}_3]} &= \frac{Q_m[\text{Ca}^{2+}]_m - Q_b[\text{Ca}^{2+}]_b}{Q_b} \\ &= \text{CoC}[\text{Ca}^{2+}]_m - [\text{Ca}^{2+}]_b\end{aligned}\quad (1)$$

Here, Q_m and Q_b are the makeup and blowdown water flow rates (in m^3/s), CoC is the cycles of concentration (ratio of makeup and blowdown water flowrates) and $[\text{Ca}^{2+}]$ is the calcium ion concentration expressed in terms of calcium hardness (in mg/L as CaCO_3). The numerator represents the amount of calcium precipitated in the whole circuit (in g/s of CaCO_3), it is divided by the blowdown water flow rate so as to have a common indicator compatible with both pilot-plant and power-plant scales.

2.3. Test campaign

Moreover, the overall campaign was conducted by maintaining one pilot plant as a reference (module No.4), where no polymer was added, and the other three modules were treated using polymers (modules No.1 to 3, respectively). The test campaign lasted from October 2014 to April 2015, implying a variable water calcium loss (ΔCa) during the whole campaign attributed to changes in river water quality. For compensating these variations and comparing the effects of polymers regardless of water quality, the overall efficiency of ASP η_{ASP} is defined as follows:

$$\eta_{\text{ASP}} = 1 - \frac{\Delta\text{Ca}_{\text{ASP}}}{\Delta\text{Ca}_{\text{ref mod}}}\quad (2)$$

with $\Delta\text{Ca}_{\text{ASP}}$ representing the water calcium loss in the module operating with polymer, and $\Delta\text{Ca}_{\text{ref mod}}$ representing the reference module operating under the same conditions but without polymers.

Two sequential series of tests were performed using the four pilot plants. For comparing the efficiencies of the ASPs, three commercial polymers were used, one per module, under the same operating conditions (temperature, flow rate, and concentrations) for 9 weeks. The main available characteristics of the three ASP polymers are as follows: an acrylic acid copolymer of 4000 g/mol (ASP1), an acrylic acid homopolymer of 2000 g/mol (ASP2), and a carboxylate copolymer of 2000 g/mol (ASP3). During the second phase (10 weeks), ASP1 was used in all three modules for model calibration. During the whole campaign, cycles of concentration were maintained constant at 1.6, and the difference of temperatures in the cooling tower was 10°C . The investigated influence parameters are the polymer concentration in ppm of active matter, hot temperature (at the condenser outlet), and the amount of acid (for potential acid/polymer interaction). The main experimental conditions are reported in Table 1 in the Appendix, with make-up water parameters and operating conditions of the pilot plants, calcite saturation ratio Ω (i.e., the ratio of ion activity product and calcite equilibrium constant K_{sp}) reported in Table 1 have been calculated using PHREEQC software.

As the objective of the campaign is not to obtain zero scaling but rather to observe the inhibition of growth, scaling has to be observed during the campaign. This leads to polymer efficiencies of less than 100%. However, as the campaign lasted for several weeks, we did not want to induce massive scaling in the reference module; hence, sulfuric acid (0.18 mol/L) is always injected in all pilot plant units together with polymers so as to limit the observed scaling. It was required to adjust the acid flow rate to the variations of river chemistry; its addition is aimed at controlling the water chemistry in the cooling circuit and testing the potential dependency between the polymer efficiency and water alkalinity.

3. Modeling growth inhibition

3.1. Precipitation kinetic modeling in absence of inhibitor

For modeling the inhibition of growth by polymers, a model for the precipitation of CaCO_3 without polymers is required. The in-house “CooliSS” software (Alos-Ramos et al., 2008) is employed herein, coded as a Scilab



toolbox (Rapenne et al., 2013), with the possible use of a graphical interface. An overview of the CooliSS software is provided online as Supplementary Material, with the contributions of Alos-Ramos et al. (2008); Marconnet et al. (2014) and Mabrouk et al. (2015). In brief, the software utilizes a canonical chemical engineering approach for representing physicochemical phenomena in circuits. Chemical equilibria are modeled using the PHREEQC software (Parkhurst and Appelo, 1999). The model uses a rate-based formulation, considering the kinetic limitation for the precipitation or dissolution of CaCO_3 , as well as gas-liquid mass-transfer in the cooling tower for stripping as well as for the evaporation of water. The kinetics of calcium carbonate precipitation is taken from Appelo et al. (1998), which is based on an earlier model of Plummer et al., 1978. This kinetic law has been derived from laboratory measurements using ideal solutions and has been adapted by the introduction of a critical saturation index (Mabrouk et al., 2015) for accurately predicting the saturation threshold observed in recirculating cooling circuits; the modified equation is expressed as follows:

$$R_{\text{CaCO}_3} = r_f \left(1 - 10^{\frac{2}{3}(SI - CSI)} \right) \quad (3)$$

$$r_f = k_1 a_{\text{H}^+} + k_2 a_{\text{CO}_2} + k_3 a_{\text{H}_2\text{O}} \quad (4)$$

Here, R_{CaCO_3} represents the surface kinetic rate ($\text{mol.m}^{-2}.\text{s}^{-1}$, positive for dissolution and negative for precipitation), k_1 , k_2 , k_3 represent the temperature-dependent kinetic constants ($\text{m}^3.\text{m}^{-2}.\text{s}^{-1}$, see Plummer et al., 1978), a represents the activities of the species (mol.m^{-3}), $SI = \log \left(a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} / K_{sp} \right)$ represents the calcite saturation index and CSI the critical saturation index (substituted as 0.5 based on previous tests). The activities and calcite thermodynamic precipitation constant K_{sp} are calculated using the PHREEQC software.

The mass-transfer between water and air in the cooling tower is modeled using the two-film theory (similarly as in Safari et al., 2014) by considering the mass-transfer limitation and thermodynamic driving force:

$$J = K_{OL} a_{gl} (C_L - H/C_G) \quad (5)$$

With J represents the mass-transfer flux from the liquid to the gas phase ($\text{mol.m}^{-3}.\text{s}^{-1}$), K_{OL} represents the overall mass-transfer coefficient (m.s^{-1}), a_{gl} the gas-liquid interfacial area ($\text{m}^2.\text{m}^{-3}$), C_L and C_G represent the concentration in the liquid and the gas phase, respectively, and H represents the Henry's constant (-).

The pH affects the precipitation rate through the proton activity in eq. (4), its value is calculated using the PHREEQC software considering the water chemical equilibria, especially the calco-carbonic equilibrium modified by acid injection, and the release of dissolved gases to the air in the cooling tower using the eq. (5).

The reaction and stripping rates, equations (3) and (5), respectively, are valid only locally in the circuit and need to be implemented in mass balances in each equipment. Hence, a plug-flow regime is assumed in both the condenser and cooling tower, as well as perfect stirring behavior in basins and injections points. As a result, the solutions of transport, transfer, and reaction equations represent the concentrations and fluxes in the whole system.

Solving the transport, reaction and transfer equations requires the knowledge of water temperature path along the circuit as well as the water evaporation rate in the cooling tower. Experimental values can be used if these information are available to the user, thermal calculations are then performed by assuming linear temperature profiles in condenser and cooling tower and performing heat balances in each unit operation. Alternatively, a dedicated tool called TEFERI (Bourillot, 1983) can be used for thermal calculations. The program TEFERI calculates the cooling performances of cooling towers as a function of inlet water (temperature, flow rate), ambient conditions (e.g. air temperature and humidity) and the characteristics of the evaporative cooling towers provided by the packing manufacturer or by in-house measurements (e.g. Height of a Transfer Unit, HTU vs. the ratio of water-air mass flow rates). The software is based on the Poppe and Merkel methods for the calculation of evaporative cooling. For more details on cooling tower calculations, see for example the chapter dedicated to cooling towers written by Erens (2010) in the VDI Heat Atlas.

As an example of typical temperature path, the outlet condenser temperature is around 40 °C (generally between 35 and 45 °C), the outlet cooling tower temperature is around 30 °C (the cooling water temperature difference could be between 5 and 15 °C depending on cooling tower design). The water evaporative rate is around 12 kg/h for a pilot plant with a make-up flow rate of 34 kg/h, and cycles of concentration (CoC) of 1.6. These values are order of magnitude and are highly dependent on operating and ambient conditions. More details on the counter-current cooling tower design procedure and order of magnitudes of various quantities can be found in Chien et al. (2012).

On the other hand, the software has been calibrated with pilot-plant measurements and validated using industrial data from EDF nuclear power plants. Currently, this software is employed by engineers for evaluating

the impact of treatments on the cooling circuit scaling and water quality, for example, to define dynamic acid injection control strategies (Marconnet et al., 2014). Before using the CooliSS software for developing a new polymer inhibition model, it is essential to verify that these simulations accurately predict the precipitation of CaCO_3 in the absence of polymers. Hence, simulations are performed using the makeup water characteristics (concentration, temperature, and flow rate) and pilot-plant operating conditions (heat duty, temperature, cycle of concentration, acid flow rate). Experimental water calcium losses are shown in Figure 1, with corresponding simulations for the reference module without the polymer. Along the test campaigns, the agreement between simulations and experiments is satisfactory as variations (attributed to the evolution of makeup water and/or modifications of operating conditions) are accurately predicted with an average deviation of 13 mg/L as CaCO_3 (around 9% relative deviation). Given the experimental uncertainties of the water calcium loss estimated at around 15 mg/L as CaCO_3 , the model is thus considered to be sufficiently robust for supporting the complementary inhibition model.

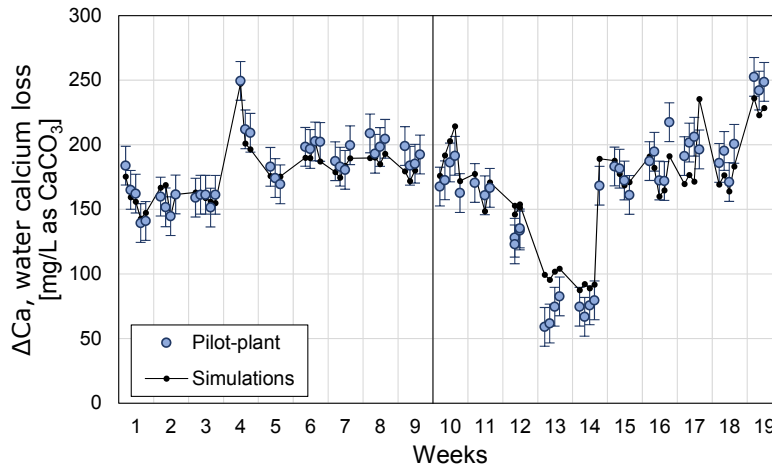


Figure 3: Comparison between experimental water calcium loss for the reference module (without the polymer) and CooliSS simulations (no fitting performed)

3.2. Inhibition model development

As explained above, the adsorption of polymers on growth sites is the main mode of action for the inhibition of scale. Hence, the kinetic rate in the presence of inhibitor $R_{\text{CaCO}_3, \text{ASP}}$ can be expressed as the kinetic rate in the absence of inhibitor R_{CaCO_3} multiplied by the fraction of available growth site $(1 - \theta)$, where θ represents the fractional coverage by the adsorbed polymers:

$$R_{\text{CaCO}_3, \text{ASP}} = (1 - \theta)R_{\text{CaCO}_3} \quad (6)$$

The kinetic rate R_{CaCO_3} has already been implemented in CooliSS software, and θ can be described by a dedicated model detailed below. Within this framework, the effects of water quality and cooling circuit operation (e.g., concentration factor and injected acid) are considered by the precipitation rate R_{CaCO_3} , mitigated by the calculation of the fraction coverage θ , dependent of temperature and inhibitor concentration. The fractional coverage phenomenon can be either the consequence of the adsorption of polymers on growth sites or the accumulation of inhibitors at the diffusion boundary in the narrow crystal growth sites (Gill et al., 1983). In both cases, polymers prevent crystal precursors from reaching the growth sites, attributed to steric hindrance and repulsive force caused by static electricity.

Laboratory-scale measurements by Lisitsin et al. (2009) as well as results obtained from the pilot-plant test campaign (see Results section), suggest a type I adsorption isotherm, typically well represented by the Langmuir adsorption model. In this paper, the mathematical model of Kubota and Mullin (1995) is utilized, which modifies the original Langmuir adsorption model by introducing an impurity effectiveness factor α to account for the effectiveness of a given impurity for growth suppression (for the physical meaning of α , please see the original paper of Kubota and Mullin, 1995). Hence, the mathematical model is expressed as follows:

$$\theta(T, [\text{ASP}]) = \alpha \frac{K_a(T)[\text{ASP}]}{1 + K_a(T)[\text{ASP}]} \quad (7)$$



$$K_a(T) = K_a^0 e^{-\Delta H_a^0/(RT)} \quad (8)$$

Here, θ represents the fractional coverage of Eq. 6 (dimensionless), α represents the effectiveness factor (dimensionless), $[ASP]$ represents the ASP concentration (in mg/L of active matter), K_a represents the Langmuir equilibrium constant (here in L/mg) whose dependency on temperature is given by Eq. 8, K_a^0 is the pre-exponential factor (in L/mg), ΔH_a^0 is the standard enthalpy change (J/mol), R represents the ideal gas constant (J/mol/K) and T represents the absolute temperature (K). The three parameters α , K_a^0 and ΔH_a^0 are identified by experimental measurements obtained during the test campaign.

4. Results and discussions

4.1. Experimental results

In the following sections, the reported polymer concentration is the overall concentration injected in the circuit (in ppm of active matter), which should not be confused with its residual concentration in water. Figure 4 shows the water calcium loss ΔCa during the test campaign (see the Appendix for details on the operating conditions and river water quality during the whole campaign).

Comparison of polymer efficiency. The first phase aims to compare the ASP efficiency of three commercial polymers: ASP1, ASP2, and ASP3; the efficiency can be observed by comparing the water calcium loss in the circuits treated with polymers (pilots 1–3) and that in pilot 4 without the polymer. As shown in Figure 4 (top), ASP1, ASP2, and ASP3 exhibit comparable efficiencies and similar responses to changes in operating conditions such as polymer concentration, temperature, and water chemistry. Despite experimental uncertainties (estimated around 15 mg/L as $CaCO_3$), ranking is observed, with ASP1 being the most efficient; this ranking can be explained by the differences in the polymer characteristics such as chemical functions and molar mass (as illustrated by Jada et al., 2007; Al-Hamzah et al., 2014); however, it is difficult to proceed with the analysis with the marginal information given by polymer suppliers.

Nucleation inhibition and growth inhibition. Irrespective of the polymer chosen, a sharp increase for the water calcium loss is observed between weeks 3 and 4, shifting from a null calcium balance (i.e., 100% polymer efficiency) to positive values; this shift matches the increase of the calcite saturation ratio of the makeup water during the week end between those weeks (see Appendix), without the adaptation of the acid flow rate. Furthermore, notably, there is no return to the original state as similar operating conditions before and after this event lead to different water calcium losses. Conditions are similar during week 2 (outlet condenser temperature of 40 °C, 3 ppm of ASP) and weeks 8 and 9 (outlet condenser temperature of 40 °C, ASP concentrations of 2.5 and 4 ppm, respectively), and the water calcium losses during week 2 are almost equal to zero in the three pilot plants with ASP, and between 50 and 120 mg/L during weeks 8 and 9. This observation is interpreted as a change in the mode of action of the polymer. As indicated in the introduction, the polymer can prevent the appearance of crystalline germ, i.e., inhibits nucleation or limits crystalline growth, that is, inhibits growth kinetics. Initially, with the cleaned pilot plants, the addition of polymers was probably sufficient for preventing nucleation for three weeks. However, with a higher saturation index, the nucleation energy barrier decreases; hence, it is necessary to increase the polymer concentration, and it is difficult to reach the concentration threshold. Consequently, it is assumed that the polymer acts as a nucleation inhibitor during the three first week, while the circuit was clean, then acts as a crystal growth inhibitor once nucleation occurred, attributed to a high residence time of the water in the recirculating circuit and a high calcite saturation ratio.

Effect of operating parameters on polymer efficiency. The individual effect of operating parameters is observed by gathering data obtained under identical conditions. The overall efficiency of ASP polymer η_{ASP} is plotted in Figure 5 with respect to the polymer concentration (Figure 5, top) and condenser outlet temperature (Figure 5, bottom), with other parameters maintained constant while screening the investigated parameter. As shown in Figure 5 (top), the ASP efficiency rapidly increases with polymer concentration and reaches a constant value after 4 ppm. However, the efficiency decreases with increasing temperature, as shown in Figure 5 (bottom). These two observations, already observed previously (Al-Hamzah et al. 2014; Sparks et al. 2015), reinforce the choice of an adsorption model as adsorption is favored at low temperature, and Figure 5 (top) is similar to a type I adsorption isotherm.

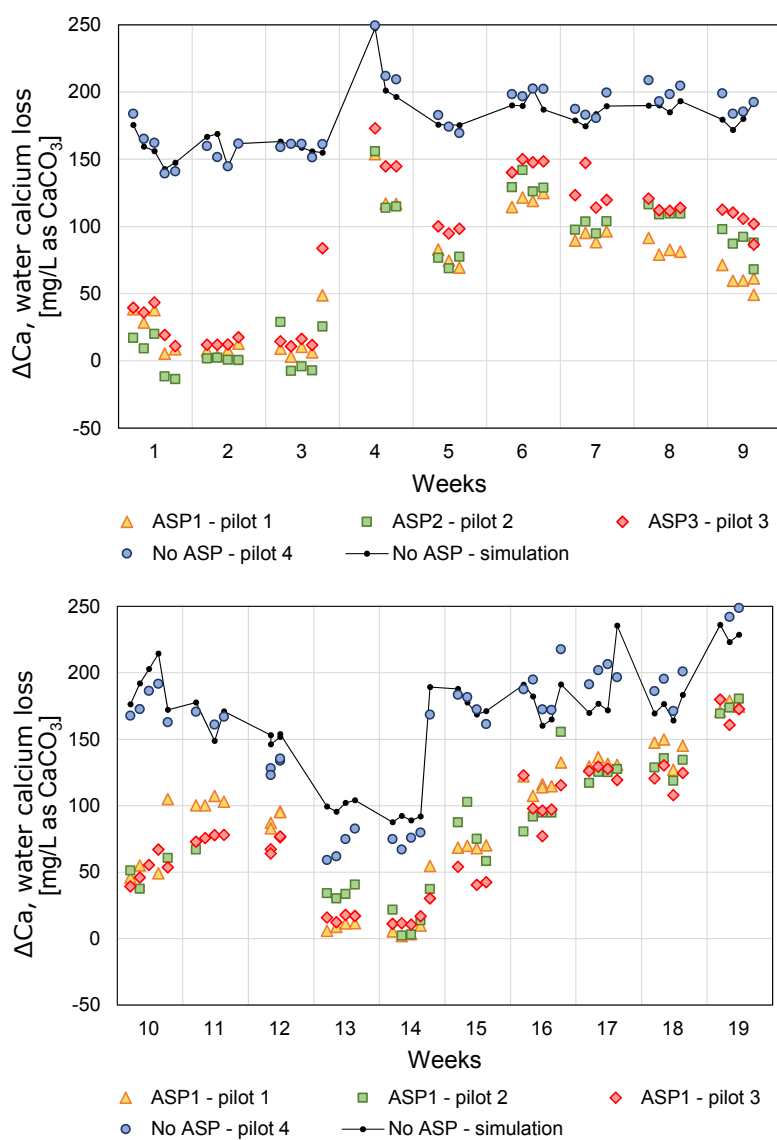


Figure 4: Results of water calcium loss during the first phase (top) for comparison of polymer efficiency, and the second phase (bottom) for parametric screening (experimental uncertainties, estimated around 15 mg/L, are not shown for the purpose of readability)

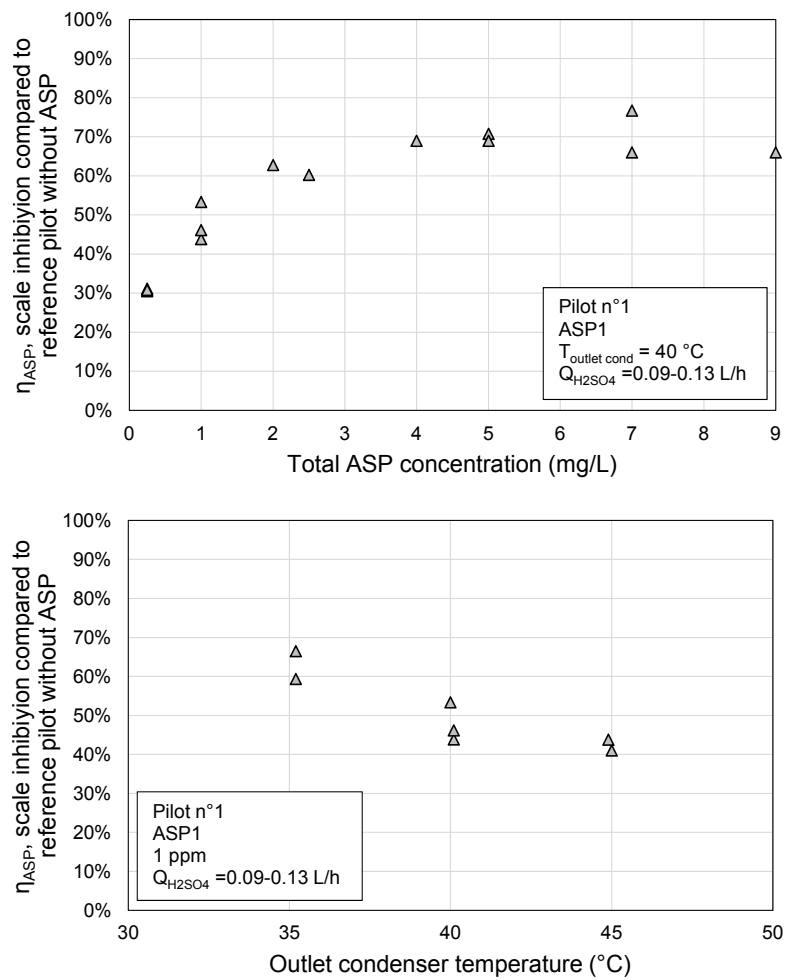


Figure 5: Effect of polymer concentration and, condenser outlet temperature on the overall efficiency of an antiscalant polymer

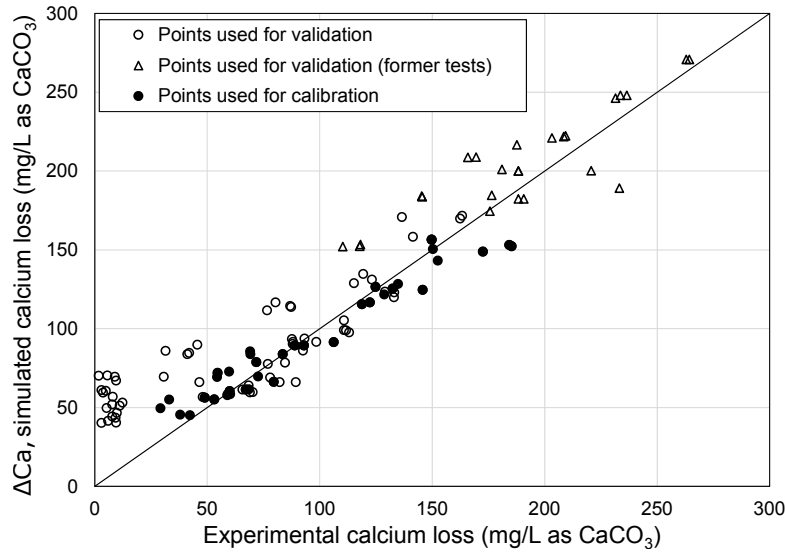


Figure 6: Parity plot of predicted vs. experimental water calcium loss for all data. Closed points from 2014 to 2015 are used for model calibration, while other points are used for model validation

4.2. Modeling results

As ASP1 exhibits higher efficiency, it was used in the second series of experiments in the three pilot plants. The goal was to acquire more data for the parametric identification of the model using the ASP1 polymer. Three parameters, the effectiveness factor α , pre-exponential factor of the Langmuir equilibrium constant K_a^0 and the standard enthalpy change ΔH_a^0 (see equations 7 and 8) are to be identified. The effectiveness factor α is assumed to be constant; however, it could represent a function of the physicochemical properties in a further version of the model. In total, 37 points are selected among the stabilized data for covering the concentration range from 0.25 to 9 ppm and the temperature range in the circuit from 20 to 45°C, and the three parameters regress with a least-square method on water calcium loss. The optimal set of parameters for ASP1 is as follows:

$$\begin{cases} \alpha &= 0.97 \\ \ln K_a^0 &= -33.26 (K_a^0 \text{ in } \text{L.mg}_{\text{ASP}}^{-1}) \\ \Delta H_a^0 &= -91.8 \text{ kJ.mol}^{-1} \end{cases} \quad (9)$$

The average absolute deviation between regressed and experimental data is 10 mg/L as CaCO_3 for the 37 chosen points; hence, a satisfactory fit is obtained as the deviation is below the experimental uncertainties. For validating the model, 43 additional points from the campaign are considered, as well as 25 points from a former campaign in 2012. The points from the former 2012 tests are obtained under more constraining conditions; the cycles of concentration were high, with less or no acid at all, and more alkaline river water compared to the 2014-2015 tests. Figure 6 shows the parity plot representing calcium losses for the simulated and pilot plant water for all 105 points. The points used for regression are well distributed along the first bisector in the regression range between 30 and 180 mg/L, as well as the validation points in the same range. In extrapolation, the points are also well distributed for a high water calcium loss, corresponding to the 2012 tests under conditions prone to the precipitation of calcite. However, the model tends to overpredict water calcium losses in the low-scaling region as it simulates scaling around 50 mg/L as CaCO_3 , whereas no scaling is practically observed on pilot plants. For all 105 points, the average absolute deviation between measurements and simulations is 21 mg/L as CaCO_3 .

Figure 7 shows the comparison between the water calcium loss obtained with ASP1 on pilot plant 1 (same values as on Figure 4) and the corresponding simulations with CoolISS software, modified with equations (6) to (8) and parameters of equation (9). As the circuit was clean during the three first weeks, simulations are not performed for the period as the model is not adapted; hence, a nucleation model could be used instead. The model accurately reacts to changes in river water quality as well as modifications of operating parameters, except for two weeks (13th and 14th) where the software predicts a positive water calcium loss, but no scaling is observed on pilot plants. These weeks correspond to the points of higher deviations in Figure 6 in the low-scaling region at high acid flow rate, suggesting a missing interaction in the model construction (see discussions on model limitations).

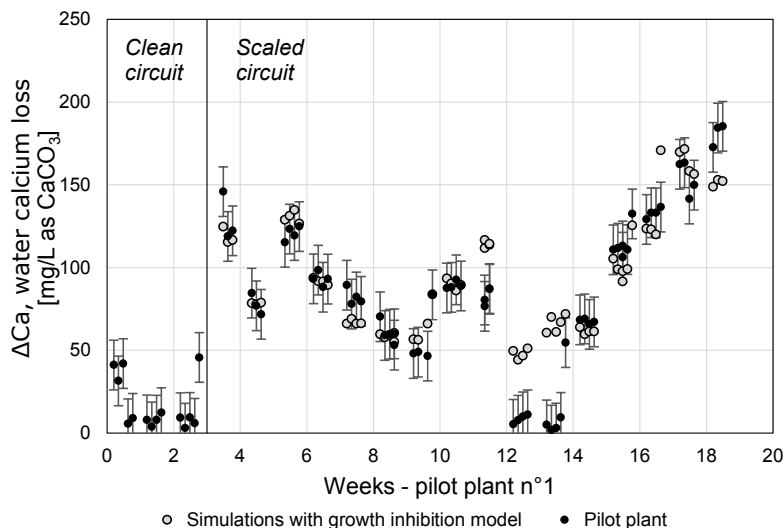


Figure 7: Experimental water calcium balance and CooliSS (modified with ASP inhibition model) simulations for all the data of pilot 1

4.3. Comments on recirculating cooling circuits

Effect of polymer treatment. As mentioned earlier, two of the main characteristics of recirculating cooling circuits are the salt concentration by water evaporation (represented by the cycles of concentration, CoC) and the important water residence time, attributed to the large water volume in the recirculation loop. The higher the CoC, the higher the calcite saturation ratio in the circuit. If Ω_{river} represents the calcite saturation ratio in the river, the saturation ratio in the circuit would then be $CoC^2 \times \Omega_{river}$ in the absence of scaling. This increase of the saturation ratio lowers both nucleation and crystal-growth thermodynamic energy barriers. In addition, the mean residence time is typically around a few hours, which is quite superior to the calcite induction period. In the pilot plants, the mean residence time was set to 5 h, implying that it takes at least a day to evacuate 99% of inlet salts, considering a first-order response, i.e., assuming that the circuit is a stirred tank without dead volumes (which is obviously not the case). In comparison, the induction period is estimated between 3 and 15 min during the test campaign using the formula from He et al. (1999).

Owing to both thermodynamic and kinetic aspects, maintaining a clean recirculating cooling circuit would be possible for low CoC and/or low saturated waters. The minimal polymer dose could be estimated by the models reported by Vanderpool (2006) or He et al. (1999). In other cases, the polymer acts as a growth inhibitor with efficiencies described herein. According to equation (7), the fractional growth sites coverage θ approaches α (very close to 1) at high polymer concentrations; θ represents the relative amount of inaccessible growth sites, caused by the presence of the polymer, either by the direct adsorption of the polymer or by electrostatic repulsion. However, the relationship between θ and the inhibition of calcite precipitation in the circuit η_{ASP} is not linear, and a fractional coverage of $\theta = 0.5$ would not lead to a 50% inhibition efficiency. For illustrating this point, Figure 8 shows the antiscalant efficiency, systemically measured for pilot plants, versus the mean fractional coverage calculated by the model for all tests. The water calcium loss exhibits a moderate decrease with fractional coverage (i.e., overall efficiency increase), followed by a stiff increase above a fractional coverage of 0.8. This nonlinear curve is caused by the plug-flow regime in the condenser and cooling tower, and the reaction rate is integrated along the flow path; hence, the concentration exiting such equipment is not proportional to the reaction rate, but it follows a logarithmic evolution. This result explains the nature of the dependency between fraction coverage, which directly modifies the kinetic rate, and the observed efficiency in the circuit. The complete curve shown in Figure 8 is obtained with CooliSS by manually modifying the value of θ from 0 (no coverage) to 1 (full coverage).

Complementary effect with acid injection. The injection of acid, as a stoichiometric treatment of water alkalinity, would lead to excessive use of chemicals for cooling circuits with high-scaling issues. Hence, the addition of a few parts per million of polymers would result in an adverse decrease in the precipitation of calcium carbonate. For instance, Figure 9 shows the (normalized) amount of acid to inject in the circuit for maintaining scaling below an arbitrary water calcium loss of 30 mg/L as $CaCO_3$, for three river water hardness values. For soft water (dotted curve), a small amount of acid is required to limit scaling without the polymer (a fifth of the

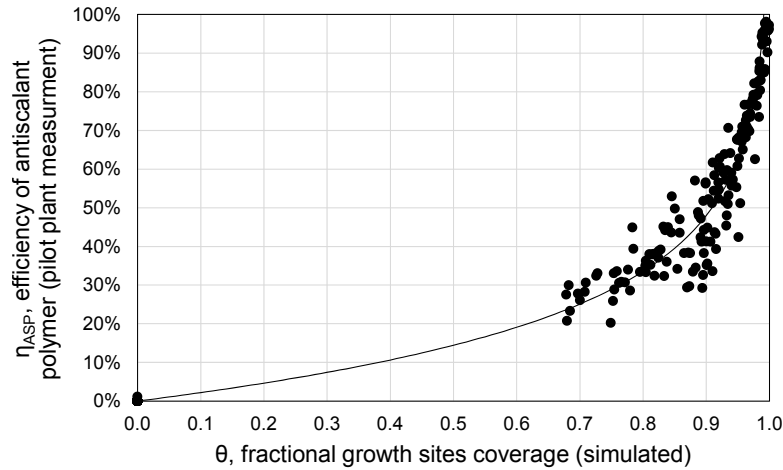


Figure 8: Link between the value of θ and the precipitation inhibition

amount for hard water), and the addition of polymer decreases this amount to zero after 2 ppm. Moreover, for moderately hard water (dashed curve) and hard water (plain curve), the addition of polymer also decreases the acid flow rate, but acid is still required even for high polymer concentration, attributed to the adsorption plateau. For hard water, a combination of both treatments would probably be the most effective and economic for limiting scaling without the consumption of large amounts of chemicals and polymer injection complemented by acid injection as 100% efficiency with only use of polymers is difficult to achieve because of the adsorption plateau.

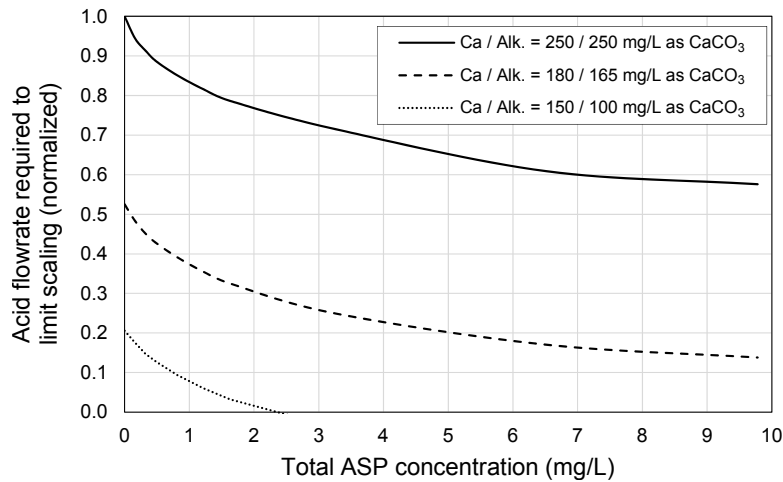


Figure 9: Examples of the trade-off between polymer and acid injection to maintain scaling below a water calcium loss of 30 mg/L as CaCO_3 , simulated for several river water hardness

4.4. Model limitations and further development

The developed model allows for the prediction of the efficiency of the chosen ASP with respect to the cooling circuit design, make-up water quality, and operating conditions. Although the model is validated for an extended range of water qualities and operating conditions, experimental results are representative for pilot plants with specific surface materials and suspended solids in the Seine river natural water. Further development is required for enhancing model predictability, including the effect of surfaces (e.g., concrete, heat exchanger metallic surfaces, plastic packing, and suspended matter) and additional water properties on model parameters for ensuring better transposability from one circuit to another. For example, discrepancies between simulations and experiments (see Figure 7) suggest the dependency of the pH on the polymer efficiency. For instance, Wisniewska et al. (2014) have reported the effects of solution pH on the adsorption isotherms of polyacrylic acid (PAA) on mixed silica alumina, caused by the modification of surface charge density; Sparks et al. (2015)



have reported the effect of pH on the energies of adsorption of PAA on calcite. Hence, the adsorption model could include such dependencies, in addition to temperature and polymer concentration.

In addition, it would be interesting to investigate the effect of the polymer characteristics (e.g., repeat units, structure, and molar mass distribution) on model parameters. This would let us limit the need of a long test campaign on pilot plants for new polymers. For instance, Kubota and Mullin (1995) have investigated the crystal growth of KBr in the presence of aliphatic carboxylic acids and found that the effectiveness factor α increases with the carbon number of the acid, while the adsorption equilibrium constant K remains nearly constant. Such quantification between polymer properties and antiscalant efficiency would allow for the estimation of the model parameters with laboratory-scale measurements; nevertheless, the chemical nature of the antiscalants would need to be known.

5. Conclusions

This study provides comprehensive knowledge on the antiscalant efficiency of polymers in a recirculating cooling circuit by using industrial pilot plants and natural river water as the coolant. Three commercial polymers were tested, and they exhibited comparable antiscalant efficiencies and similar responses to changes in operating conditions. This study demonstrates the characteristics of a recirculating cooling circuit, where the inhibition of calcite occurs because of crystal-growth inhibition rather than nucleation inhibition, attributed to the high saturation ratio and long residence time in the system.

The results obtained from the industrial pilot plant are in agreement with laboratory-scale observations, particularly the identification of crystal-growth inhibition by an adsorption mechanism. In addition, interesting insights on scale mitigation are obtained for pilot plants, such as the non-linear relation between the fraction growth-site coverage and the scale inhibition in the circuit. The use of an industrial pilot plant is critical for accurately simulating a full-scale cooling circuit and scale inhibition.

The developed adsorption model related the raw river water quality and process operating conditions (e.g., cycles of concentration, temperatures, and amount of treatments) to the ASP efficiency. This model could be used to design treatments and define control strategies. The model could be improved to consider the dependency of model parameters to additional operating parameters such as solution pH and to the polymer nature.

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Supplementary data

Supplementary material related to this article (overview of the original CooliSS software, i.e. without polymer addition) can be found online at [10.1016/j.desal.2016.06.018](https://doi.org/10.1016/j.desal.2016.06.018).

Appendix: experimental conditions during tests



Table 1: Experimental conditions (weekly averaged) during the test campaign; three different ASP were used during the first phase (efficiency comparison, weeks 1 to 9), and only ASP1 was used during the second phase (parametric screening, weeks 10 to 19)

Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Make-up water																			
Calcium (mg/L as CaCO ₃)	247	212	225	263	254	253	257	255	251	247	262	239	256	260	255	250	248	246	245
Alkalinity (mg/L as CaCO ₃)	200	195	201	239	230	230	230	227	226	233	238	224	237	232	226	224	217	216	212
pH	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.3	8.3	8.3	8.3	8.2	8.2	8.2	8.1	8.1	8.1
Suspended solids (mg/L)	7	12	7	10	8	4	4	11	7	20	10	18	8	20	20	9	8	20	17
Conductivity (µS/cm)	444	445	473	529	527	522	533	532	537	507	528	494	520	538	539	519	519	526	519
Calcite saturation ratio (IAP/K_{sp})	10.1	8.4	9.6	13.7	11.6	11.8	11.6	12.1	11.9	12.2	13.7	11.9	13.6	11.5	11.9	10.4	8.9	8.7	8.0
Operating conditions																			
CoC	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
T _{out, condenser} (°C)	45	40	35	45	40	45	40	40	40	40	40	40	40	40	35	35	45	45	40
T _{out, cooling tower} (°C)	35	30	25	35	30	35	30	30	30	30	30	30	30	30	25	25	35	35	30
QH ₂ SO ₄ 0.18 M (L/h)	0.10	0.07	0.07	0.10	0.10	0.11	0.10	0.10	0.11	0.10	0.14	0.13	0.25	0.22	0.10	0.10	0.10	0.10	0
[ASP] pilot 1 (ppm)	3	3	3	2	2	1	1	2.5	4	5	1	0.25	1	0.25	1	0.25	1	0.25	0.5
[ASP] pilot 2 (ppm)	3	3	3	2	2	1	1	2.5	4	7	2	0.50	2	0.50	2	0.50	2	0.5	1
[ASP] pilot 3 (ppm)	3	3	3	2	2	1	1	2.5	4	9	3	0.75	3	0.75	3	0.75	3	0.75	2
[ASP] pilot 4 (ppm)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0