New Stable Biodegradable Scale Inhibitor Formulations for Cooling Water: Development and Field Tests

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ABSTRACT

The increased demand for more sustainability of inhibitor systems in open cooling water circuit applications has dominated much of the development activity in this area in recent years. Biodegradability has been a top priority in this context due to ever more restrictive legislation in Europe regarding the discharge of chemicals into flowing waters.

Various biodegradable scale inhibitor formulations based on biodegradable carboxylic acids have been developed recently and exhibit good scale inhibition performance in pilot plant tests along with low toxicity and reasonable raw material cost. The widespread use of such systems throughout the industry has thus far been prevented by a fundamental concern: depending on circuit conditions, biodegradation of inhibitors may commence within the cooling systems as opposed to the desired degradation after discharge. Consequently, inhibition performance will be diminished and additional problems with increasing biological activity in the circuit are posed. The necessary countermeasures would be increased dosages of oxidizing biocides which in turn would diminish the effectiveness of the inhibitors, thereby substantially reducing the environmental and financial customer benefit.

A novel water treatment composition by Henkel Surface Technologies counteracts this effect, combining good biodegradability of the discharged inhibitors with high inhibition performance at low concentrations in conjunction with effective biological control. We present field tests from an industrial plant in Germany which clearly show the enhancement of overall performance derived from the full integration of scale inhibition and biological control treatment programs.

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. Due to the very low solubility of e.g. calcium carbonate and calcium sulfate (solubility products $CaCO_3$: 4.9×10^{-9} mol^2l^{-2}, $CaSO_4$: 7.1×10^{-5} mol^2l^{-2}), precipitation readily takes place and causes severe problems in operation, functionality and lifetime of mechanical equipment, thereby directly translating into increased cost. Since the removal of scale-forming cations (e.g. Ca, Mg, Ba) from process waters is not a feasible approach if large volumes are used, water treatment products are widely used to prevent the formation of deposits. The majority of state-of-the art products for the prevention of both calcium carbonate and sulfate scaling in flowing water systems is based on phosphonic acids and polycarboxylates. They are usually distinguished by excellent efficiency in conjunction with low human and aquatic toxicity. Additionally, their long-term ecological behavior is well documented owing to considerable recent research efforts[1-7]. General risk assessments have shown that these substances do not represent a risk for the environment[8-9]. However, the poor biodegradability and P-content of these compounds have become an increasing reason for concern. Free discharge of poorly biodegradable phosphonic acids or polycarboxylates into running waters at industrial levels represents a considerable burden on the environment, and regulations on the use and consequently, legislative restraints on the discharge of water treatment chemicals have become increasingly stringent. Therefore, an ever-increasing demand for environmentally compatible, fully biodegradable inhibitor systems has arisen[10-12]. In accordance to the principles of responsible care, a general product profile for ecologically benign inhibitor systems has been developed[13] :

- Excellent (state-of-the-art) scale inhibition
- Low aquatic and human toxicity
- High biodegradability
- Not subject to labeling
- Low water hazard class (max. 2)
- Good price/performance ratio
- Free of phosphorus

Since none of the currently employed state-of-the-art products fulfill all of these demands, new scale inhibitor systems have recently been developed to close this gap[13], the most promising of which are based on polyaspartic acid.

In addition to these properties, a biodegradable scale inhibitor product will have to prove under field conditions that the desired biodegradability after discharge will not in conjunction pose a biological control problem during retention time within the system, namely premature biodegradation before discharge. This would be expected to increase both microorganism contamination and decline product efficiency by bacterial consumption, thereby reducing the effectively available product concentration. For flow-though systems such as encountered in mining operations and neutralizing plants, the field-readiness of polyaspartate-based scale inhibitors has already been demonstrated[10, 13]. It is the aim of this work to show that this also holds true for open cooling circuits with a considerably higher holding time index.

The work presented here will outline both the basic performance evaluation of polyaspartate-based scale inhibitors giving a short review of laboratory scale development. The successful transfer to pilot plant scale and a subsequent field study at an industrial plant facility are discussed in detail and universally show the status of polyaspartates as fully functional for industrial use as part of an integrated treatment concept in conjunction with standard biological control.

EXPERIMENTAL

FAST LABORATORY SCREENING TESTS

Different fast screening tests have been employed in order to ensure rapid evaluation of experiments and therefore speed up the assessment of new scale inhibitors. Calcium sulfate and calcium carbonate inhibition are assessed separately by a static bottle test ($CaSO_4$) and a dynamic heat-exchange circulation method ($CaCO_3$).

$CaSO_4$-inhibition (static bottle test) : A standardized Na_2SO_4-solution is mixed with a standardized $CaCl_2$-solution and the scale inhibitor into a sealable duran glass flask. The respective concentrations (see Table 1 below) are chosen to be above the solubility range of $CaSO_4$, utilizing a higher overall concentration for a fast evaluation of raw materials. Assessment of inhibitor performance is determined by observing the turbidity of the respective solution as a function of time. The relative efficiency is then calculated by a weighted average.

Tab. 1 : Experimental parameters for static bottle testing of $CaSO_4$ scale inhibition

Experiment conditions		
Temperature	30 °C	68^{o}F
pH	8.5 [1]	8.5 [1]
Test Time	24h	24h
Ion concentrations		
Ca^{2+}	100 mol/m^3	10,000 ppm $CaCO_3$
SO_4^{2-}	100 mol/m^3	9,610 ppm
Na^+	166 mol/m^3	3818 ppm
Cl^-	166 mol/m^3	5,893 ppm
Inhibitor concentration (mg/l)	5,10,15,20,25	5,10,15,20,25

[1] adjusted by NaOH

$CaCO_3$-inhibition (dynamic scaling test) : A standardized synthetic process water containing the inhibitor to be tested is pumped for a defined time at constant flow rate through a helical glass tube heated to constant temperature (usually 80^{o}C). After the testing time, the tube is completely purged with a defined amount of dilute HCl. The

calcium carbonate inhibition efficiency is then assessed by comparing the titrimetric Ca-content of the purge solutions with the reference values (without inhibitor).

Table 2 summarizes the basic parameters of the dynamic carbonate scaling experiment. A schematic representation of the test apparatus is shown in Fig.1.

Table 2 : Experimental parameters for dynamic testing of $CaCO_3$ scale inhibition

Experiment conditions			
Temperature	(°C)	40-90°C	
Flow rate	(l/h)	0.5	
Test Time	(h)	1-2	
Test solution		mol/m^3	ppm $CaCO_3$
Ca^{2+}		5.4	540
Mg^{2+}		1.8	180
TAC (m-value)		20	1000
Inhibitor concentration (mg/l)		2,4,6,8,10	

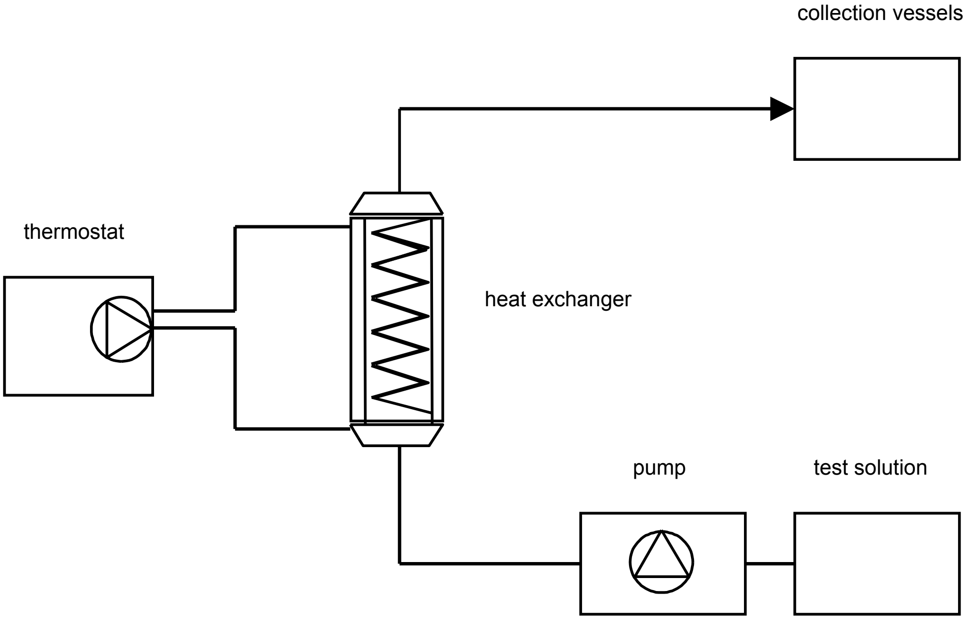

Fig. 1 : Schematic representation of laboratory testing apparatus for $CaCO_3$-Inhibition (dynamic heat exchanger method)

Dispersant efficiency (spectroscopic low-solids dispersion test) : The dispersant efficiency of the inhibitor formulations was evaluated using a newly developed spectroscopic testing method. This method has been described in detail elsewhere[14], and shall therefore be reviewed here only briefly. As opposed to conventional dispersant testing methods operating in the g/l-regime of solid content (i.e. methods based on light scattering), our technique can operate at solid contents below 200 mg/l.

Controlled synthetic water is mixed with a predetermined amount of insoluble solid test material (typically kaolin or iron oxide). Different inhibitors are compared by measuring extinction vs. time at controlled temperature at a wavelength λ=460 nm as measured with a conventional spectrophotometer. The slope derived from linearization of the curves characterizes the dispersants efficiency. Normalization of these data against the blind value determined without inhibitor provides the Relative Dispersant Efficiency of the investigated additive, which yields an accurate ranking.

POLYASPARTIC ACID

Different polyaspartic acids with varying mean molecular weights, molecular weight distributions, degrees of branching and purity have been investigated. Since there are several pathways along which polyaspartic acids are produced in bulk quantities (e.g. solid phase thermal condensation of aspartic acid, catalyzed polymerization of aspartic acid, reaction of maleic acid with ammonia[15-21]), a wide variety of different qualities are readily available. Fig. 2 displays the general chemical structure.

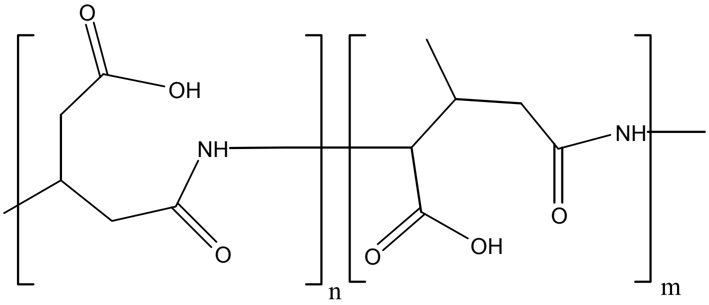

Fig. 2 : Chemical structure of polyaspartic acid

RESULTS AND DISCUSSION

POLYASPARTATES : LABORATORY SCALE INHIBITION TESTS

$CaSO_4$ scale inhibition : Fig. 3 shows the results of screening tests for calcium sulfate scale inhibition using the static bottle testing method. Polyaspartate exhibit excellent inhibition efficiency comparable to state-of-the-art polyacrylate. Note that the phosphonate is completely ineffective against $CaSO_4$ scales.

$CaCO_3$ scale inhibition : Fig. 4 depicts the concentration dependence of several new scale inhibitors compared to a state-of-the-art phosphonate as measured by the dynamic heat exchanger method.

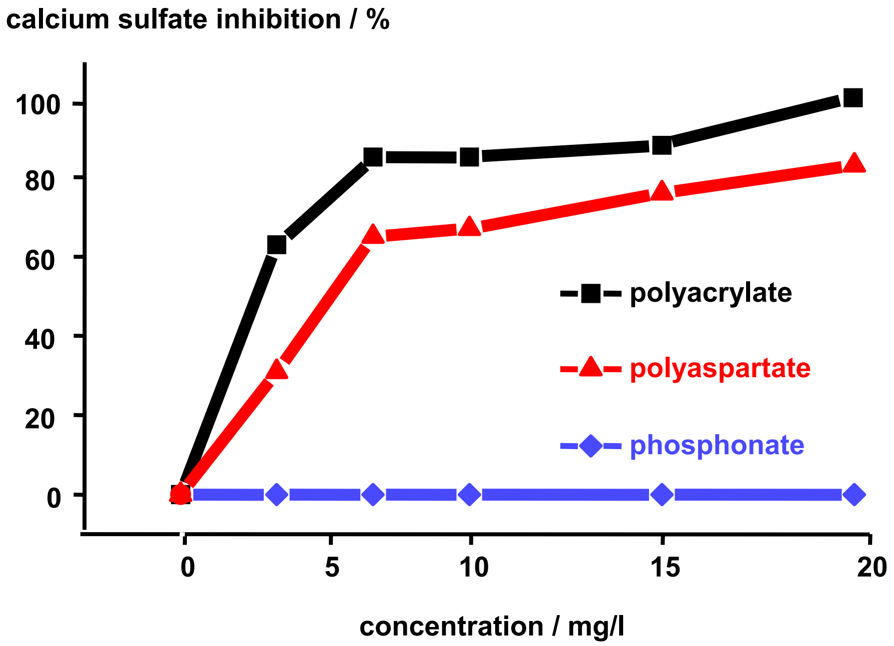

Fig. 3 : Calcium sulfate scale inhibition as measured by static bottle testing method. Concentration dependence is shown at 30°C.

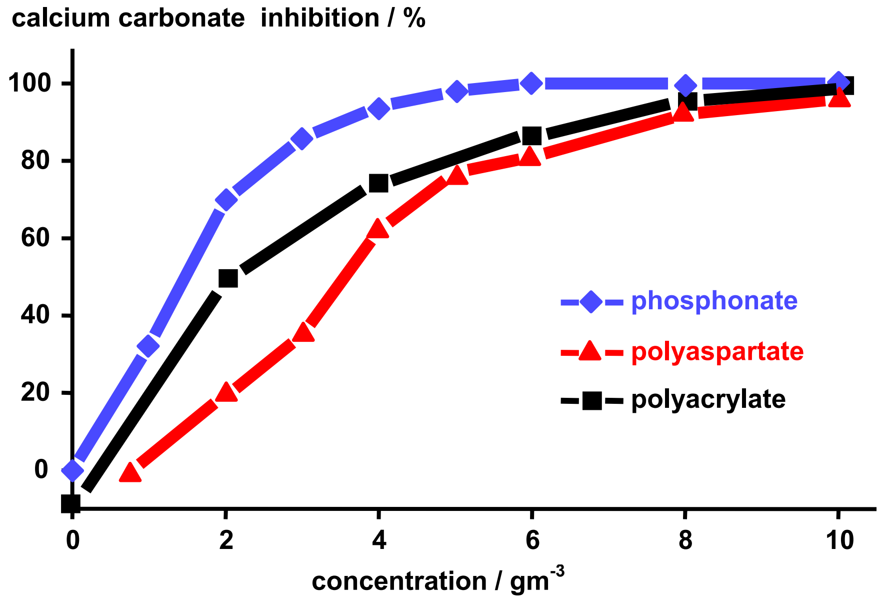

Fig. 4 : Calcium carbonate scale inhibition as measured by dynamic heat exchanger testing method. Concentration dependence is shown at

Several of the substances tested exhibit a carbonate stabilization efficiency approaching 100 % at the concentration plateau equal to the phosphonate standard. However, Fig. 4 also shows that the phosphonate reaches its plateau of maximum performance at lower concentration levels. The performance of the polyaspartate is comparable to classical polyacrylate systems in carbonate stabilization. In general, the performance plateau levels between 5 and 10 ppm of inhibitor dosage observed here are within the normal treatment envelope for industrial cooling water systems. Consequently, the ecological benefits of the new inhibitor systems should pose a clear advantage for water treatment products.

POLYASPARTATES : DISPERSANT EFFICIENCY

The most stringent product definitions for new scale inhibitor systems dictate that besides universal applicability to the prevention of the most common scales in industrial water treatment (as demonstrated above for polyaspartates) a good dispersant efficiency should also be achieved. This is of fundamental concern when operation is to be extended to cooling systems with a high amount of suspended solids such as encountered with suddenly changing water conditions, operating under very hard water conditions or treating multiple stages or facilities of a single industrial installation with an integrated water treatment concept. We have therefore evaluated the dispersant properties of the same polyaspartate from the scaling tests, using the spectroscopic low-solids testing method described in the experimental section. Fig. 5 displays the dispersant efficiency of the polyaspartate-based formulation 8413-3 for two different solids as compared to a polyacrylate and a phosphonate :

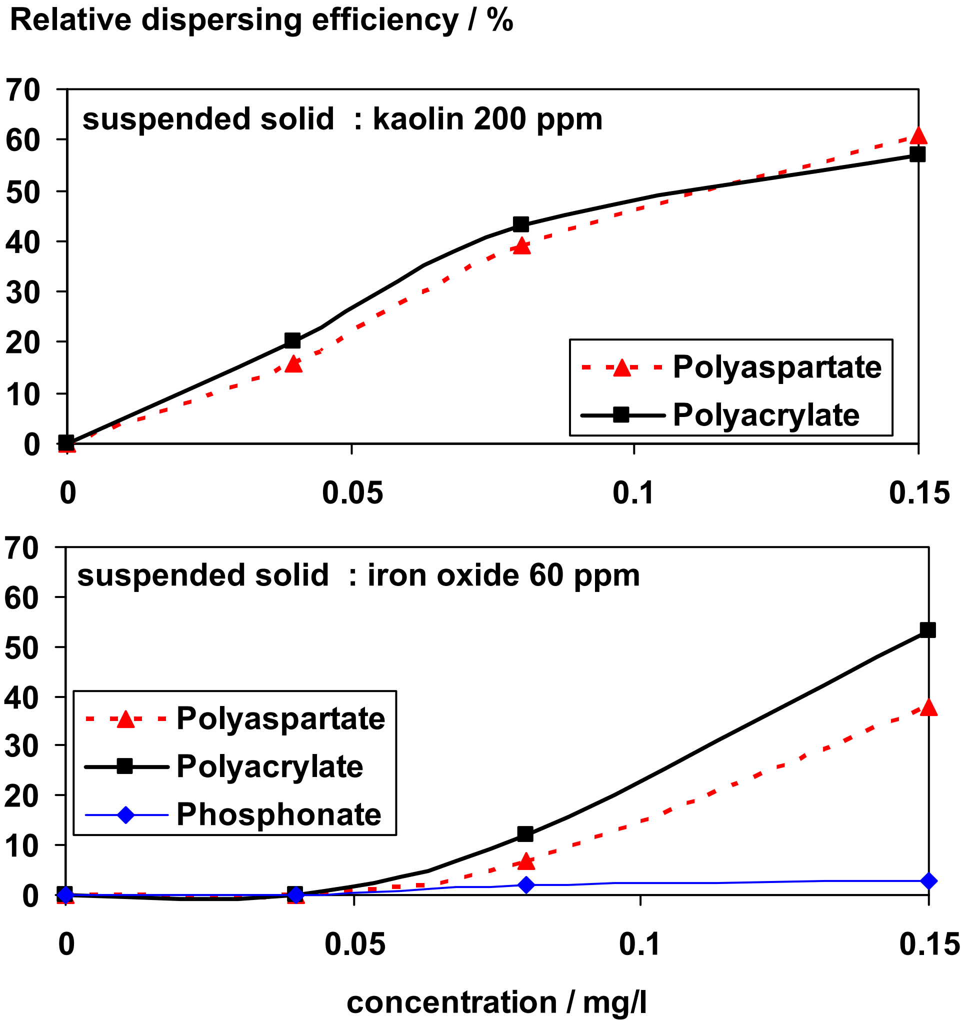

Fig. 5 : Relative dispersing efficiency of a polyaspartate-based formulation 8413-3 for two different solids in comparison to a conventional dispersants.

Fig. 5 shows that the performance of the polyaspartate closely matches the reference system. We can therefore conclude that all laboratory testing methods for both scale inhibition and dispersion effeiciency show a very promising performance profile for the polyaspartate-based formulation. In the next section, we will investigate the scale-up of a new polyaspartate based product to the pilot plant scale.

PILOT PLANT TRIALS

The telling questions to be answered in the pilot plant trials regarding the polyaspartate formulation are clearly defined :

- Does the high efficiency in lab tests translate into the pilot plant ?
- Is microbiological growth promoted by the formulation ?
- Does degradation occur within the system ?
- Can biocide treatment neutralize these possible side effects ?

The pilot cooling tower used in our experiments is depicted in Fig. 8 and closely emulates all relevant elements of an actual industrial facility. The total water volume of the system is $1m^3$. The temperature difference in the heat exchanger amounts to $\Delta T=10^oC$ (18 °F). T_{max} in the system is 25^oC. The system is configured as an evaporating cooling tower. The make-up water replacing the losses can be taken from different water qualities. System blow-down is controlled by conductivity measurements and is kept at a variable preset level. A typical holding time index $T_{1/2}$ of approximately 35 h was chosen. Scale formation is measured on exchangeable steel heat exchanger tubes. For each trial, a new stainless steel heat exchanger tube is put in. Upon trial conclusion (typically 14-21 days), tubes are removed and cut in half. The section facing the highest thermal load is used for gravimetrical determination of the deposit amount, another part for chemical analysis of the deposit. For the experiments described here, inhibitor dosage was kept at 10 mg/l in the primary cooling water.

Fig. 6 : Pilot plant cooling circuit

Two different water qualities were used in this study, labeled “standard” and “moderate”, respectively. Table 3 summarizes the properties of the test water.

Table 3 : Water qualities used for pilot plant trials

	Ca (ppm $CaCO_3$)	m-value (ppm $CaCO_3$)	pH	conductivity (µS/cm)	LSI
Make-Up Water	220 - 260	180 - 220	7.3 – 7.6	770 - 850	0.0 – 0.2
Standard Water	370 – 420	290 – 315	8.4 – 8.6	1200 - 1350	1.6 – 1.7
Moderate Water	340 – 360	260 – 280	8.4 – 8.6	100 – 115	1.5 – 1.6

The results from the scaling tests using different treatment programs are summarized in Table 4 (The deposits consist primarily of $CaCO_3$):

Table 4 : Scaling efficiency results of pilot plant trials

a) Standard Water

Treatment program	**$T_{1/2}$ (h)**	**Deposit (g/m^2)**
None	35	394
8441 (Phosphonate/Polyacrylate)	35	20
8413-3 (Polyaspartate)	35	14
8413-3 (Polyaspartate) [1]	35	40
8413-3 (Polyaspartate)	70	62

[1] TAC (m-value): 330 ppm $CaCO_3$ (6.6 mol/m³)

b) Moderate Water

Treatment program	**$T_{1/2}$ (h)**	**Deposit (g/m^2)**
None	35	210
Standard Phosphonate Program	35	10
8413-3 (Polyaspartate) Trial 1	35	13
8413-3 (Polyaspartate) Trial 2	35	5
8413-3 (Polyaspartate)	70	25

Clearly, the performance of the polyaspartate product easily reaches the standard at both water qualities. The additional stress put on the product by a longer holding time index was also investigated. For this, the make-up water was blended with 50% DI water, thereby effectively achieving an increased cycle of concentration and a doubled $T_{1/2}$. The data indicate a slight increase of the deposit amount.

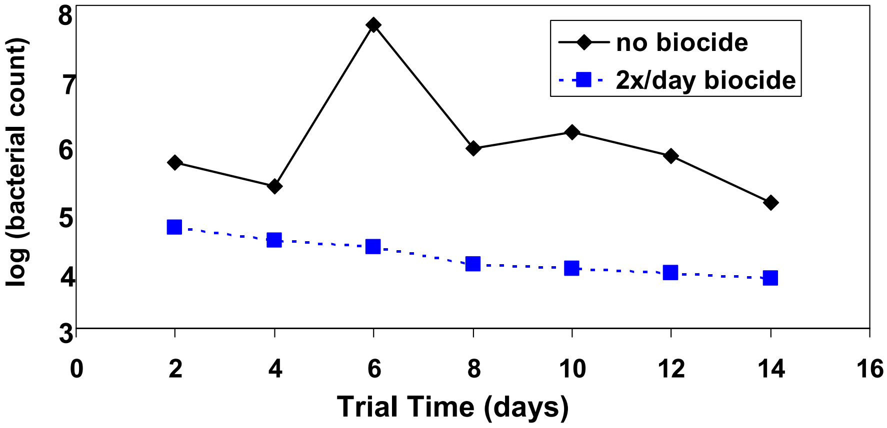

Fig. 7 : Typical bacterial count during trial

It is noteworthy that a significant effect of additional biocide dosage on microbiological growth was found in the experiments. This is evident from Fig. 7, in which the monitored bacterial count in the system is depicted with and without biocide treatment. This also has the expected effect on product loss within the pilot circuit. Table 5 summarizes the observed losses of polyaspartate with and without biocide treatment.

Table 5 : Polyaspartate product loss with and without biocide treatment

	max. loss (%)	min. loss (%)
Without biocide	82	75
With biocide	42	20

Table 5 clearly shows the product loss with biocide addition to be at the same level as encountered for state-of-the-art non-biodegradable treatments.

We therefore conclude that under normal water conditions a full replacement of polyacrylate formulations with polyaspartate should be possible. Microbiological control is advised to control the bacterial growth and to avoid high product loss. This treatment process has been developed into a marketable product lately and has been patented by us. Depending on application conditions, most notably plant specifications, holding times and water qualities, it is advised that specific treatment concepts be developed for each customer case. This concept is naturally facilitated by the array of versatile and fast laboratory and pilot plant testing methods described herein. The subsequently described case study at an industrial facility in Germany shows that this is indeed the case.

CASE STUDY

An array of 5 separate open cooling circuits with a single central makeup water and inhibitor dosage facility at a German industrial plant served as the initial customer trial for the polyaspartate-based formulation 8413-3. The system had previously been successfully treated by a phosphonate based anti-scaling program. However, the strict water discharge policy of the local government made a switch towards a completely biodegradable system desirable. An additional difficulty was posed by the target of doubling the thickening factor of the circuit water from 2 to 4. Table 6 summarizes plant parameters :

Table 6 : Initial and target parameters at the cooling circuits

Plant Parameter	**Initial State**
System volume (m^3)	90
Water recirculation (m^3/h)	700
Make-up water (m^3/h)	14
Evaporated water (m^3/h)	7
Blow-down water (m^3/h)	7
Temperature Difference (K)	7
Cold Water Temperature (^oC)	8
Warm Water Temperature (^oC)	15
Cycle of concentration	2 → 4

The treatment concept we devised was to encompass the best possible scale prevention along with efficient dispersion of any suspended solids and elimination of sludge deposits. Additionally, safe control of microbiological parameters was to be achieved within the pH range of 7.5 to 9. An additional difficulty was posed by the non-constant production cycles, which could lead to plant standstill in dependence on demand.

The solution to the problem was a proprietary combined treatment concept using the polyaspartate-based scale inhibitor/dispersant *P3-ferrofos®8413-3* along with the environment-friendly contact biocide *P3-ferrocid® 8590*. The following treatment parameters were finally advised to the customer :

Table 7 : Treatment parameters advised to customer

Parameter	**Value**	
pH	< 9	
Ca^{2+}	< 800 ppm $CaCO_3$	< 6.4 mol/m^3
TAC (m-value)	< 320 ppm $CaCO_3$	< 6.4 mol/m^3
Suspended solids	< 10 ppm	< 10 mg/l
In-Circuit inhibitor concentration	10-30 ppm	10 – 30 mg/l
Biocide dosage interval	2x / week	
Biocide dosage concentration	150 ppm	150 mg/l

During the initial trial phase, the water parameters were monitored separately for all circuits and the replenishment water and found to be within specifications. Table 8 shows some typical values :

Table 8 : Water parameters during trial phase

Parameter	**unit**	**Make-up Water**	**Cooling Circuits**				
			1	**2**	**3**	**4**	**5**
pH		**7.7**	**8.6**	**8.6**	**8.5**	**8.5**	**8.7**
conductivity	**µS/cm**	**269**	**1205**	**991**	**647**	**694**	**1073**
	mS/m	**27**	**120**	**99**	**65**	**70**	**107**
t-hardness	**ppm $CaCO_3$**	**120**	**550**	**460**	**300**	**340**	**560**
	mol/m^3	**1.2**	**5.5**	**4.6**	**3.0**	**3.4**	**5.6**
Ca^{2+}	**ppm $CaCO_3$**	**90**	**320**	**290**	**190**	**250**	**410**
	mol/m^3	**0.9**	**3.2**	**2.9**	**1.9**	**2.5**	**4.1**
TAC (m-value)	**ppm $CaCO_3$**	**80**	**260**	**240**	**180**	**230**	**205**
	mol/m^3	**1.6**	**5.2**	**4.8**	**3.6**	**4.6**	**4.1**
Cl^-	**ppm**	**15**	**73**	**53**	**29**	**27**	**47**
	mg/l	**15**	**73**	**53**	**29**	**27**	**47**

The final treatment results after the trial phase are shown in Fig. 8. Obviously, no scaling has occurred on any part of the cooling systems. Additionally, heat exchanger efficiency was maintained on a high level. Biological monitoring showed total bacterial counts well within specifications. The excellent result of the trial phase has subsequently led to a complete shift of the system towards the new treatment concept. The cooling system has thus far been running for 12 months according to specifications. Scaling is still not observed.

Fig. 8 : Pictures of the cooling system described in the text after 3 months of polyaspartate/biocide treatment

CONCLUSIONS

The work presented herein clearly shows that the polyaspartate-based scale inhibitor systems show excellent performance in laboratory-scale experiments as well as pilot plant. A proprietary treatment process combining polyaspartate based scale-inhibitor and biocide treatment has proven its efficacy in a filed trial at an industrial recirculating cooling system.

REFERENCES

[1] L. Huber, *Tenside Surfactants Detergents* 12,6 (1975) 316

[2] J. Steber, P. Wierich, *Chemosphere* 15,7 (1986), 929

[3] P. Schöberl, L. Huber, *Tenside Surfactants Detergents* 25 (1988) 99

[4] S. Held, *Textilveredlung* 24,11 (1989), 394

[5] K. Fischer, *Wat. Res.* 27,3 (1993), 485

[6] W.E. Gledhill, T.C.J. Feijtel in : *Handbook of Environmental Chemistry*, Vol. 3, Part F (Detergents) , Springer Verlag, Berlin (1992) 261

[7] H. Raschke, H.-G. Rast, R. Kleinstück, H. Sicius, D. Wischer, *Chemosphere* 29,1 (1994) 81

[8] Screening Information Data Set (SIDS), *OECD Assessment Internat. Reg. of Potentially Toxic Chemicals 3*, United Nations (1996), 439

[9] J. Steber, W. Hater in : *Chemie im Kraftwerk 1997*, Essen 1997

[10] W. Hater, *Proc. Corrosion/98*, NACE, Houston (1998)

[11] B. Mayer, W. Hater, M. Schweinsberg, *Proc. Corrosion/99*, NACE, Houston (1999)

[12] M. Schweinsberg, B. Mayer, W. Hater, *Proc. EUROCORR ´99*

[13] W. Hater, M. Schweinsberg, B, Mayer, *PowerPlant Chemistry* 2(12) (2000) 721ff., 752ff.

[14] W. Hater, B. Gluesen, U. Pegelow, M. Schweinsberg, PowerPlant Chemistry 5(1) (2003) 37ff

[15] C.S. Sikes, A. Wierszbicki, *Corrosion/94*, Paper #193

[16] R.J. Ross et al., *International Water Conference 1995*, Paper#16

[17] A.J. McMahon et al., *Corrosion/95*, Paper #32 (1995)

[18] K.C. Low et al., in *Advances in Chemistry* No. 248 (Ed. J.E. Glass) (1996)

[19] R.J. Ross et al., *Material Performance* (1997,4), 53 ff.