Polyaspartate, a New Alternative for the Conditioning of Cooling Water

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Laborelec undertook tests on its pilot installation for cooling waters in order to determine under what conditions polyaspartate, a biodegradable polymer, can be used to condition the water of the cooling circuit of a power plant. The results of the pilot tests showed that the efficiency of the tested polyaspartate is similar to the one of a low molecular weight polyacrylate. Following the pilot tests, an on-site full-scale test was carried out in the cooling circuit of a power plant in June-July 2003. Traditionally, this cooling circuit is conditioned with a low molecular weight polyacrylate. Moreover, sulfuric acid is used to decrease the alkalinity of the water. During the test, polyacrylate was replaced by polyaspartate in order to verify the conclusions of the pilot tests. The test was successful from every point of view. An environmental and economic analysis of the different processes has been done and it clearly appears that polyaspartate is an interesting alternative for the conditioning treatment of large cooling circuits. A new cooling water conditioning method, based on polyaspartate, will be implemented in this power plant.

1. Introduction

Cooling circuits are generally treated against deposits of minerals (carbonates, sulphates) and suspended matter (clays). Various scale inhibitors and dispersants can be used to this end, occasionally in combination with an acid which allows the alkalinity of the water to be reduced.

Where large cooling circuits are involved, such as those in power plants, the products used must be selected so as to be cost-effective and to have minimal impact on the environment.

Polyacrylate satisfies these various conditions rather well. It disperses suspended matter well and inhibits the precipitation of calcium carbonate and calcium sulphate. It is used in small quantities, generally several milligrams per litre, which makes its operating cost acceptable. Furthermore, its toxicity towards aquatic organisms is relatively low. Conversely, it is practically non-biodegradable and therefore accumulates in the environment.

Tests were carried out in a pilot plant with a view to comparing the efficacy of a commercial polyaspartate (biodegradable product) in inhibiting calcium carbonate precipitation with that of a commercial polyacrylate. A test was then carried out at Amercoeur power plant, where the cooling circuit is normally treated with a polyacrylate. The first results of this test are given in this publication.

2. Chemistry and Properties of Polyaspartates

Polyaspartate is a polypeptide derived from aspartic acid, an amino acid naturally present in proteins. There are several methods for obtaining polyaspartate, namely[3,4]:

- thermal condensation of aspartic acid,
- catalysed polymerisation of aspartic acid and
- thermal polymerisation of maleic acid and ammonium hydroxide.

These three reactions give rise to an intermediary compound, polysuccinimide, which is transformed into polyaspartate by alkaline hydrolysis. Fig. 1 represents polyaspartates.

The structure and chemical characteristics of polyaspartate will vary depending on the method used to obtain it. Principally, the mean molecular weight, the distribution of molecular weights, the formation of branched structures, the purity of the product and its properties are synthesis-dependent.

Polyaspartates are dispersants[1], like poly-acrylates, and adsorb onto suspended matter. Polyaspartates also inhibit the precipitation of calcium carbonate[1-4], calcium sulphate[2,3] and barium sulphate[3,4]. The optimum molecular weights to inhibit the precipitation of calcium carbonate and barium sulphate are 2-4 kg/mol.[3]. For calcium sulphate, the optimum molecular weight is 1-2 kg/mol.[3]. Like polyacrylates, polyaspartates act by threshold effect, in other words they act at concentrations significantly lower than stoichiometry.

Polyaspartates are highly biodegradable and their biodegradability depends largely on the method of synthesis and the linearity of the polymeric chain[1]. Polyaspartates are considered to be rapidly biodegradable according to OECD standard 301B[2,3]. They are also not very toxic according to data provided by polyaspartate suppliers.

Finally, polyaspartates would be sensitive to chlorine because of the nitrogen-carbon links contained in their molecule. Nevertheless, no data has been found in the literature on this subject. The various suppliers of polyaspartates contacted indicate either an insensitivity to chlorine or a slight sensitivity to high concentrations of free chlorine.

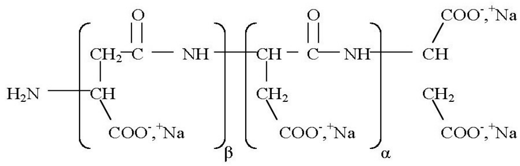

Fig. 1. Structure of polyaspartate[1].

3. Comparison of Polyaspartate and Polyacrylate in a Pilot Plant

Before beginning an on-site test with a new product, it is essential that its various properties are verified in a pilot plant, in conditions as close as possible to those that will be encountered in situ. The various properties tested are the inhibiting effect on the precipitation of calcium carbonate, resistance to chlorine and the acceleration of biological growth.

3.1. Description of the pilot plant The MERADES pilot loop (Module d'Etude et de Recherche Appliquée Des Eaux de Surface – Surface Waters Applied Research and Study Module) comprises two independent circuits. Each circuit is made up of a mechanical-draught cooling tower, a "condenser" consisting of four exchanger tubes with a total length of 32 m, a makeup water circuit and a blowdown water circuit. All parameters can be adjusted. The quality of the waters (in the makeup and in the circuit) is constantly monitored. The measurements of conductivity, pH, alkalinity, calcium hardness, total hardness, chlorides, etc. are forwarded to a supervision monitor. The same is true of the measurements of pressure, temperature and flow rate. Fig. 2 shows a functional diagram of the pilot installation.

3.2. Procedure for determining the inhibiting effect on calcium carbonate The experiment parameters (maximum temperature at condenser outlet, concentration factor, condenser heating, flow rate, etc.) are constantly adjusted and are identical for the two circuits in the installation.

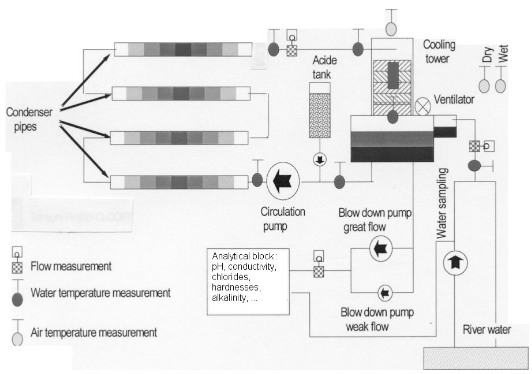

Fig. 2. Functional diagram of the MERADES installation (one circuit).

The inhibitor is continuously injected into the makeup water to obtain the desired concentration (one circuit is treated with polyaspartate, the other with polyacrylate). Sulphuric acid is injected into the circuit to keep the pH below 8.3 at the start of the test. The injection of sulphuric acid will be gradually reduced until the phenomenon of calcium carbonate precipitation appears.

The precipitation is monitored by chemical assessment. In a circuit where there is no precipitation, the following equation is continuously verified:

$$\frac{C_C}{C_M} = \frac{CaH_C}{CaH_M} = \frac{TH_C}{TH_M} = \frac{Cl_C}{Cl_M} = k$$

In this relationship index C is relative to the circuit water and index M to the makeup water. CaH and TH represent the calcium hardness and the total hardness. Cl represents the concentration in chlorides. In the case of precipitation, the following inequality is respected:

$$\frac{CaH_C}{CaH_M} < \frac{TH_C}{TH_M} < \frac{Cl_C}{Cl_M}$$

As soon as the difference between the chloride concentration factor and the calcium concentration factor is greater than 0.1 unit, precipitation is evident. The limiting chemical characteristics corresponding to the precipitation point are then determined. This involves the following parameters: CaH, M-Alk, pH and SAL factor.

The SAL factor is given by the relationship:

$$SAL = M\text{-}Alk^2 * CaH / f$$

In this relationship the M-Alk and CaH are expressed in French degrees (1°f = 10 ppm CaCO3). f is the ionic force factor as defined in the counterbalancing CO_2 equation of Zehender, Stumm and Fischer[5]. The SAL factor is used for the acid treatment of several Belgian power plants.

3.3. Test results The tests were carried out in parallel on the two independent circuits of the pilot plant, one treated with 7 mg/l of polyaspartate (commercial product with 40% polyaspartate, mean molecular mass 3 kg/mol.) and the other treated with 5 mg/l of polyacrylate (commercial product with 30% polyacrylate, mean molecular mass 1 kg/mol.). These tests were carried out under conditions similar to those in the cooling circuit of Amercoeur power plant, namely:

- Canal water
- Concentration factor = 1.7 to 2.0
- Condenser output temperature 30 to 38°C
- Increase in temperature at condenser = 8.5°C
- Hydraulic half-time of circuit = around 20 h
- High-efficacy film-type cooling tower fill

The chemical data at the moment of precipitation are given in tables 1 to 4 and are summarised in Fig. 3.

The following conclusions may be drawn from these calcium carbonate precipitation tests:

- The scale inhibiting efficacies of the two commercial products tested are comparable, polyaspartate being slightly more effective at the lowest temperatures in this test.
- Temperature has a non-negligible effect on inhibiting efficacy.
- The calcium concentration has a relatively minor influence. It was impossible to correlate the SAL factor to the temperature at the moment of precipitation. Conversely, as can be seen in Fig. 3, the M-ALK at the moment of precipitation may be correlated to the temperature. Acid treatment based on a M-ALK-temperature relationship can therefore be envisaged.

Throughout the tests, the total bacterial flora was measured on an agar-agar substrate in the two circuits and in the makeup water to check whether the use of polyaspartate increased biological growth compared to the use of polyacrylate. The results of these measurements are given in Fig. 4.

As we can see, the two circuits contain large amounts of bacteria, often more than 10^6 CFU/ml. Circuit 1, treated with polyaspartate, often contains more bacteria than circuit 2 (treated with polyacrylate). Nevertheless, this difference is relatively minor, therefore not significant.

Injections of chlorine (sodium hypochlorite), in the amount of 20 mg/l of Cl_2, were carried out in the two circuits at regular intervals. No drop in efficacy was visible during the injections. Conversely, the measurements of residual inhibitor concentrations were systematically falsified by the presence of residual chlorine.

Finally, a visual inspection did not reveal any difference between the two circuits. The accelerated formation of biofilm, which could have been a fear where polyaspartate was used, could not be highlighted.

Table 1
T° = **30°C** (condenser outlet)

	polyaspartate	polyacrylate
SAL	30229	29099
CaH (ppm $CaCO_3$)	523	528
TH (ppm $CaCO_3$)	600	605
M-Alk (ppm $CaCO_3$)	340	332
Cl^- (ppm Cl^-)	103	104
pH	8.82	8.78
Concentration factor	1.75	1.77
Langelier Index	2.1	2.0
Ryznar Index	4.7	4.7

Table 2 T° = **34°C** (condenser outlet)		
	polyaspartate	polyacrylate
SAL	32878	29663
CaH (ppm $CaCO_3$)	579	583
TH (ppm $CaCO_3$)	668	669
M-Alk (ppm $CaCO_3$)	327	319
Cl^- (ppm Cl^-)	112	113
pH	8.81	8.78
Concentration factor	1.79	1.80
Langelier Index	2.2	2.1
Ryznar Index	4.5	4.6

Table 3 T° = **36°C** (condenser outlet)		
	polyaspartate	polyacrylate
SAL	24137	27772
CaH (ppm $CaCO_3$)	574	605
TH (ppm $CaCO_3$)	659	688
M-Alk (ppm $CaCO_3$)	300	303
Cl^- (ppm Cl^-)	126	129
pH	8.76	8.71
Concentration factor	1.91	1.97
Langelier Index	2.1	2.1
Ryznar Index	4.6	4.55

Table 4 T° = **38°C** (condenser outlet)		
	polyaspartate	polyacrylate
SAL	24807	23922
CaH (ppm $CaCO_3$)	574	565
TH (ppm $CaCO_3$)	654	643
M-Alk (ppm $CaCO_3$)	294	291
Cl^- (ppm Cl^-)	119	121
pH	8.78	8.76
Concentration factor	2.03	1.97
Langelier Index	2.3	2.1
Ryznar Index	4.2	4.5

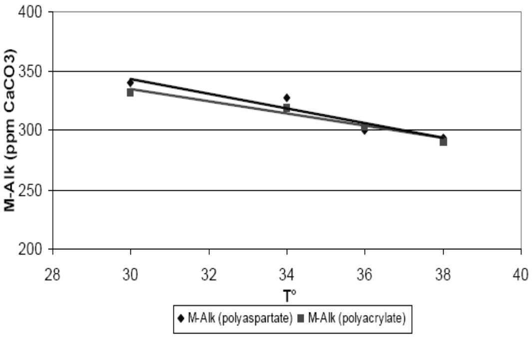

Figure 3 : tests in pilot plant
Limiting M-Alk according to condenser outlet temperature

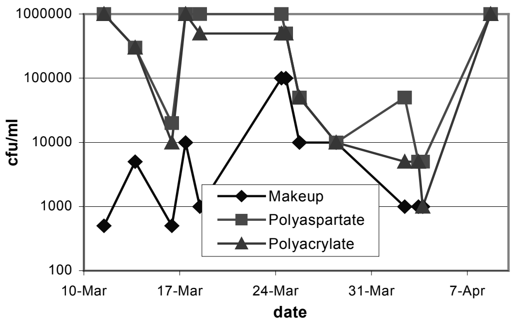

Fig. 4. Total Bacteria Counts

4. Power Plant Test

The tests were carried out in June-July 2003 at Amercoeur power plant, where the cooling circuit has the following characteristics:

- Canal water
- Volume: 8,000 m^3.
- Circulation rate: 16,500 m^3/h.
- Evaporation rate at full load (135 MW): ±200 m^3/h.
- Concentration factor: 1.9.
- Hydraulic half-time (T1/2): ±22 hours (for 250 m^3/h of purge).
- Delta T° main condenser (design): 8.5°C (at 135 MWe).
- Condenser outlet temperature: max. 38°C.
- Continual condenser cleaning system.
- Condenser tubes: Admiralty brass.
- Natural-draught counter-current cooling tower.
- Fill: fibre-cement sheets.

This circuit is generally treated with 5 mg/l of commercial polyacrylate and sulphuric acid. The acid injection is normally regulated to limit the SAL factor to 17,000 and the pH to 8.5.

During the first phase of the test (from 20 May to 15 June), the conditioning remained the same while the various parameters of the circuit were measured. During the second phase of the test (from 13 June to 15 July), the polyacrylate was gradually replaced by 7 mg/l of commercial polyaspartate. The acid conditioning remained the same.

Fig. 5 shows the results of the measurements of calcium hardness, m-alkalinity and chlorides in the circuit water. The measurements of pH and conductivity are shown in Fig. 6.

Although it was not possible, because of the acid regulation and the low salinity of the canal water, to obtain CaH and M-ALK values as high as those of the pilot tests, a certain efficacy on the part of polyaspartate can nevertheless be noted. The mean Langelier index during the test is 1.8, while the mean Ryznar index is 4.9. Under the conditions of this test, these values are impossible to maintain without the presence of a scale inhibitor.

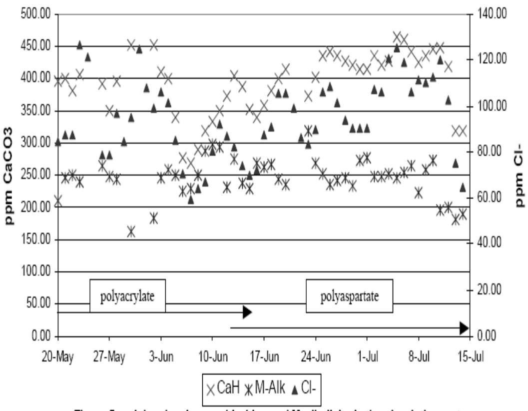

Figure 5: calcium hardness, chlorides and M-alkalinity in the circulating water (daily average)

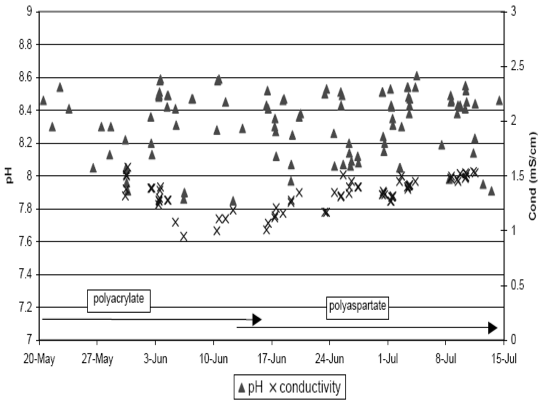

Figure 6: pH and conductivity of the circulating water

As in the tests in the pilot plant, the total bacterial flora was measured regularly. The results are shown in Fig. 7. The arrows indicate the hypochlorite injections carried out.

As can be seen, there was no increase in the mean total flora after polyaspartate was introduced. On the contrary, the tendency is even towards a reduction, although the difference is too slight to be significant.

Two of the hypochlorite injections carried out during this period were monitored more precisely.

The first took place on 03/06/2003, when the circuit was treated with 5 ppm of polyacrylate. The second took place on 01/07/03, when the circuit was treated with 7 ppm of polyaspartate.

These two hypochlorite injections were carried out under the same conditions, i.e.:

- Makeup water pump closed before start of hypochlorite injection.
- pH before hypochlorite injection = 8.5.
- Injection of 1 m^3 of sodium hypochlorite (48°Cl) in one hour.
- Makeup pump re-opened when the residual free chlorine drops below 0.5 mg/l.

If polyaspartate is attacked by chlorine, it has to consume some of it. The values for residual free chlorine and total chlorine should therefore be lower during the second hypochlorite injection. Figures 8 and 9 show that that is not the case. Furthermore, no precipitation of calcium carbonate could be highlighted by chemical analyses in the ten hypochlorite injections carried out during the power plant test. It can therefore be concluded that, under the conditions of this test, the polyaspartate tested is not sensitive to chlorine.

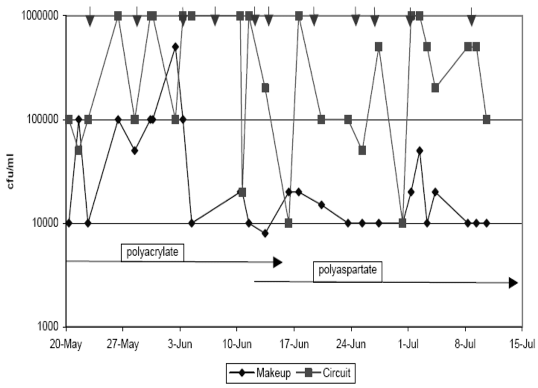

Fig. 7. Total bacteria counts.

5. Test Conclusions

From the tests in the pilot plant and in the power plant, it can be concluded that:

- Polyaspartate is as effective as polyacrylate against the precipitation of calcium carbonate.
- During these tests, polyaspartate did not affect the biological contamination of the circuit, nor the formation of biofilm.
- Under the operating conditions of the power plant and with the hypochlorite injection procedure normally used, polyaspartate is not sensitive to chlorine. It does not increase the water's chemical demand for chlorine and no

precipitation of calcium carbonate could be highlighted.

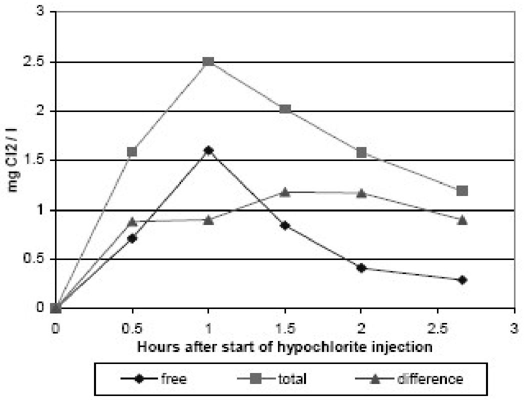

Figure 8: chlorine measured- hypochlorite injection of 03/06/03 (conditioning with polyacrylate)

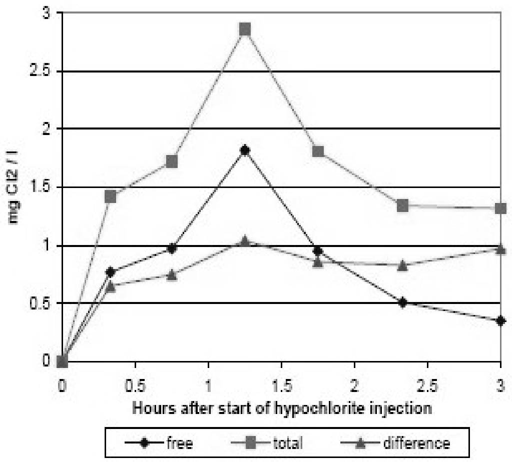

Figure 9: chlorine measured- hypochlorite injection of 01/07/03 (conditioning with polyaspartate)

6. Economic and Environmental Analysis

An analysis was carried out based on the prices of the inhibitors tested, the price of sulphuric acid and the discharge of these various products in the canal. Table 5 presents the data used for the calculations. Table 6 summarises the analysis results.

Comments: (1) The quantity of sulphuric acid is calculated to have the same protection against calcium carbonate in each case. (2) Taxes on discharges are not taken into account.

Under the operating conditions of Amercoeur power plant, the introduction of an inhibitor allows the amount of discharged sulphates to be reduced by around 100 tonnes a year but means that this inhibitor must be discharged in the canal. The use of biodegradable polyaspartate reduces the impact of this discharge in the canal but is currently the most expensive option among the solutions considered.

Table 5. Data used for the analysis.

Blowdown flowrate	200 m^3/h
Operation	300 days/year
Price of H_2SO_4	0.125 EUR/kg
Price of polyacrylate	2.5 EUR/kg
Price of polyaspartate	3.0 EUR/kg

Table 6. Analysis results (calculated).

Treatment method	Cost (EUR/yr)	Polyacrylate injected (kg/yr)	Polyaspartate injected (kg/yr)	Sulphates injected (t/yr)
H_2SO_4 only	28,000	0	0	225
5 ppm polyacrylate + H_2SO_4	33,000	7,200	0	122
7 ppm polyaspartate + H_2SO_4	45,000	0	10,080	122
Mixed treatment: H_2SO_4 + 3 ppm polyacrylate + 3 ppm polyaspartate	39,000	4,320	4,320	122

7. Final Conclusions

Anti-scale treatment of the cooling circuit is a major factor in the energy efficiency of a power plant. Furthermore, in view of the flow rates involved, the products used must be cost-effective and have as little impact as possible on the receiving watercourse.

Polyacrylate, a scale inhibitor, is widely used because it combines a high degree of efficiency at low concentrations, an affordable price and relatively low toxicity.

Pilot plant tests revealed that polyaspartate, a biodegradable product, was at least as effective against calcium carbonate as polyacrylate. A one-month test in the main cooling circuit of a power plant revealed that, under certain conditions, it could replace polyacrylate favourably.

The cost of a polyaspartate treatment is currently higher than that of a polyacrylate treatment, mainly because of the higher cost of the base product, but it allows the impact of the discharge in the canal to be limited significantly.

8. Thanks

I would like to extend my thanks to Messrs Michel Dubois, Michel Rotsaert and Jean-Pol Samain of Amercoeur power plant for their invaluable assistance and for having allowed me to publish these results.

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