Leaching of bisphenol A and F from new and old epoxy coatings: laboratory and field studies
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ABSTRACT

Laboratory tests were carried out with three types of new epoxy resins to assess the release of bisphenol A and F (BPA and BPF) and potential halogenated phenolic by-products. Tests were carried out over a duration of 6 months in the presence and absence of disinfectants (chlorine and chlorine dioxide) at realistic doses and contact times. None of the three systems exhibited Fickian-type diffusion for BPA. Leaching was quite low for two epoxies while the third showed a trend of increasing leaching during the first 5 months of immersion. BPA was only observed in the absence of disinfectant while no BPF was observed under any condition. 2,4,6-trichlorophenol (TCP), a BPA chlorination by-product was sporadically observed in the chlorinated water during the first months of contact. Following discontinuation of the disinfectants, its release was significantly enhanced in the water having been exposed to chlorinated water. Laboratory leaching tests also indicated rapid oxidation of epoxies by chlorine and chlorine dioxide. Analysis of 27 epoxy-coated drinking water storage tanks did not reveal any BPA, BPF or TCP. On the other hand, a large-scale examination of about 200 pipe sections rehabilitated with epoxies during the 1990s led to a high frequency of BPA and BPF detection, sometimes with maximum values around 1 μg/L.

Key words | bisphenol A and F, drinking water, epoxy resins, pipe rehabilitation, 2,4,6-trichlorophenol

INTRODUCTION

Epoxy resins were one of the most popular coating materials used for drinking water storage tanks in the 1980s in many countries such as the USA (AWWA 1998) and France (Bruchet et al. 1988). In terms of piping rehabilitation, although the current trend consists in laying polyurethane coatings, epoxies were frequently used in the 1990s to reline corroded pipes. In particular, the Geopox GX 014 process which was initially developed in the UK, became approved in France in the mid-1990s and was used by our French subsidiary to reline dozens of kilometres of corroded pipes. As a matter of fact, epoxy relining had completely replaced mortar-cement relining and become the relining method of choice in the UK at the end of the 1990s (Hoffman & Warren 1999).

Consumer complaints were recorded in 2008 in France, in an area with pipes relined with epoxies starting from 1995. The episode was characterised by a musty odour and a pink water colour. Gas chromatography–mass spectrometry (GC/MS) analysis revealed the presence of bisphenol A and chlorinated bisphenols, simpler phenols and halogenated phenols. Among these, 2,4,6-trichlorophenol led to its biotransformation into 2,4,6-trichloroanisole, a musty odorant with an extraordinarily low odour threshold, around 30 pg/l (Van Gemert 1999). The pipes were located in a mixing zone having water disinfected with chlorine and water disinfected with chlorine dioxide. Because bisphenol A is a known endocrine disruptor and one of thecurrently most controversial chemicals that has recently been banned in the EU for use in baby drinking bottles, this episode prompted us to reexamine the potential sanitary and organoleptic risks caused by epoxy coatings in contact with drinking water. The pink colour suggests a severe weathering, if not depolymerisation, of the epoxy resin. That this problem occurred in an area
partially disinfected with chlorine dioxide suggested accelerated ageing caused by the latter disinfectant which is already known to accelerate degradation of polyethylene pipes (Colin et al. 2009).

Epoxies are made of a polymer formed on site by reaction of a hardening agent and a prepolymer. The latter results itself from the reaction of bisphenol A on epichlorohydrin forming bisphenol glycidyl ethers, the smallest of which (bisphenol A diglycidyl ether or BADGE) has a molecular weight of 340. Heavier oligomers are also formed. In the 1980s, researchers observed the migration of epoxy oligomers including BADGE and its isomer BFDGE (bisphenol F diglycidyl ether) in networks rehabilitated with epoxy coatings, as well as dimers and trimers, and amines of the hardening agent. Bisphenol A is also mentioned as a migration product found during approval tests of material in contact with drinking water in the United States. Data from surveys of piping rehabilitation projects using epoxies, obtained by CIRSEE (Centre International de Recherche sur l’eau et l’environnement) in the early 1990s, show certain cases of migration of significant quantities of BADGE and BFDGE (unpublished data). There are only three available publications reporting the rate of bisphenol A leaching from epoxy resins: Bae et al. (2002) and Romero et al. (2002) performed static tests under laboratory conditions over a short initial period of 6 hours to 5 days, while Kosaka et al. (2002) measured the leaching rate by continuously flowing water through lined pipes over a total period of 24 months. From a health point of view, BPA is an endocrine disrupter that has been banned from polycarbonate baby feeding bottles (Official Journal of the European Union 2011). In a recent report, Anses (Agence nationale de sécurité sanitaire de l’alimentation de l’environnement et du travail) (2011), the largest sanitary agency in Europe, recognises for the first time that effects from BPA, such as alteration of sperm production, increase of ovarian cysts, brain development, lipogenesis, are well established on animals, while effects on oocyte maturation in women as well as effects on diabetes and coronary diseases on humans, are suspected.

This paper will present results from mid-term leaching tests carried out over a duration of 6 months in the absence of disinfectant and in the presence of chlorine and chlorine dioxide, as well as results from field studies both in epoxy-coated tanks and pipes.

MATERIAL AND METHODS

Three types of epoxies currently approved for use in contact with drinking water in France, the UK and the USA (E1), Spain (E2) and France (E3) were obtained as test panels from their manufacturers. All were two-component epoxies, unfortunately, the manufacturers specifications did not include any information on their chemical composition. Laboratory leaching experiments were carried out at ambient (20 ± 3 °C) temperature with a surface to volume (S/V) ratio equal to 50 cm²/l, corresponding to a small, 10–15 m³ tank. The sample bottles were kept protected from light. The panels were kept continuously immersed in mineral water (with and without disinfectant). Chlorine and chlorine dioxide levels used were 0.5 and 0.25 mg/l, respectively. The water was changed several times per week and all measurements were carried out after a stagnation period of 24 hours. Only one leaching experiment was carried out for each coating with a given disinfectant. Bisphenol A and F as well as a range of mono, di, tri and tetrachlorophenols were determined using in-situ acetylation followed by stir-bar sorptive extraction-thermal desorption-GC/MS (SBSE-GC/MS) (Nakamura & Daishima 2004). The limit of quantification (LoQ) for each analyte was equal to 10 ng/L. All samples were run in duplicate. Epoxy-lined storage tanks and pipes were sampled in the Paris and Bordeaux area between May and August 2011.

RESULTS AND DISCUSSION

Laboratory leaching tests

None of the three epoxy materials showed Fickian-type diffusion of bisphenol A (Figure 1) in non-disinfected water.

E1 only showed a few positive results above the 10 ng/l LoQ. Bisphenol A leached from E3 remained constant in the range 15–30 ng/l. E2 showed a trend of increased BPA leaching starting after 3 weeks of immersion, with a peak at 90 ng/l after 74 and 122 days. The reason for this
increase is currently unknown but this tends to indicate that official approval migration tests which are usually carried out over a period of 1 week, might not be adapted for all cases. As the manufacturers did not give any information concerning the chemical composition of their products, it is impossible to give a chemical explanation for the different behaviour of E2 compared to E1 and E3. One physical difference is that E2 is applied in a single 0.25 mm coat compared to 0.5 and 1 mm for E1 and E3, respectively. No bisphenol F was observed in any system. The two types of material which diffuse bisphenol A do so at a maximum rate of $6 \times 10^{-3} \mu g/m^2$. These rates are in the lower range of values reported by Bae et al. (2002) under the same immersion conditions (20 °C, 24 h) and are slightly lower than those reported by Romero et al. (2002) in which the migration conditions were more severe (5 days at 45 °C).

Figure 2 shows the concentrations of 2,4,6-trichlorophenol (TCP), a chlorination by-product from BPA, in the contact water from chlorinated E1, E2 and E3 coatings during the first 80 days of immersion. TCP was frequently observed in the contact waters disinfected with chlorine, in particular for E2 during the first 2 weeks of immersion. The concentration of this compound is higher than can be expected from the amount of BPA leached during this period into the non-chlorinated water (Figure 1). During the initial 2 weeks contact period, 2,4,6-trichlorophenol reaches 50–80 ng/L while bisphenol A remains at 10 ng/L in the non chlorinated water. This suggests that part of this TCP could arise from chlorine attack within the mass of the polymer. It should be remembered that epoxies do absorb between 3 and 6% of water hence the contact water chlorine can be absorbed at the same time as the water. By contrast, Kosaka et al. (2012) hypothesised that BPA and 2,4,6-TCP accumulated on the surface of the lined pipes they tested.

According to the association for research on cancer (IARC), clear evidence exists as to the carcinogenic nature of 2,4,6-TCP in animals, but which is not sufficient for humans (group 2B). The compound was therefore classified in the 2B group. The main negative side of this compound resides in its capacity to biotransform in water distribution networks into 2,4,6-trichloroanisole, a musty smelling compound which can be perceived at a 30 pg/l level (Van Gemert 1999).

No phenolic compound was detected in the presence of chlorine dioxide. Also, no BPA was detected in the disinfected waters indicating its rapid destruction by chlorine and chlorine dioxide.

**Leaching of 2,4,6-trichlorophenol after stopping the disinfection**

After 4 months of immersion, the application of the disinfectants was discontinued to check whether this could change the leaching of bisphenol A. Discontinuation of disinfection using chlorine dioxide led to an increase in bisphenol A content in the contact water from the E3 and E2 systems (see Figure 3). Comparison of Figures 1 and 3 shows that the release level of E2 in non-disinfected water is again at the same level 16 days later, i.e. 90 ng/L. Discontinuation of the disinfectant is accompanied by a cease in bisphenol A oxidation. The system’s slowness to find the...
same level as in the non-disinfected water again also suggests dioxide was absorbed by the polymer (presumably in the water absorbed by the epoxy resin) and that this supply takes around 15 days to be eliminated in the contact water. For the E1 and E3 systems, it is interesting to note that the bisphenol A content in the contact water after discontinuation of the chlorine dioxide is slightly higher than that observed in the contact water never having been disinfected. This observation, although subtle, could be a sign of deterioration of these epoxy resins, an assumption which requires confirmation through accelerated aging tests or other techniques.

Concerning the reference water which was never disinfected, BPA leaching from E2 reached a maximum at 180 ng/L (not shown) after 5 months, followed by a progressive decrease to 40 ng/L during the 6th month. The leaching experiment was stopped after 6 months.

The most clearly seen phenomenon following the discontinuation of disinfectants concerns the change in 2,4,6-trichlorophenol in the contact water for the three systems having been treated with chlorine (Figure 4).

The day after the disinfectant was discontinued, a high content level for this oxidation by-product can be seen in the contact water, varying between 0.5 μg/l (E2) to 1.25–1.47 μg/l for E1 and E3. This content level is clearly much higher than those observed in the disinfected contact water (see Figure 2). This content level then progressively decreases (Figure 4) but is again around 0.18–0.35 μg/l, 16 days after the discontinuation of chlorine. It should be remembered that this compound’s flavour threshold in water (pharmaceutical taste) is close to 0.5 μg/l (Piriou et al. 2007) and is, therefore, attained and exceeded within 24 hours following the discontinuation of chlorine for the three epoxy resins. Besides its own flavour threshold, the major disadvantage of this compound resides in its capacity to biotransform into 2,4,6-trichloroanisole.

The phenomenon observed above strongly suggests that disappearance of residual chlorine in water which is in contact with a recent epoxy coating, can contribute to enhancing the release of 2,4,6-trichlorophenol likely formed and stored within the polymer, with subsequent formation of trichloroanisole, responsible for musty odours and medicine-pharmacy. Maintaining residual chlorine appears to be an essential condition to avoid this type of phenomenon occurring.

**Indication of epoxy aging**

A yellowing of the test panels in contact with chlorine dioxide and to a lesser extent chlorine, was observed after less than 2 months of contact (Figure 5). This suggested accelerated attack of the epoxy in the presence of oxidants. Infrared spectra were acquired of the test panels surfaces after a few days of contact and were compared with spectra obtained at the end of the leaching tests. These spectra confirmed that the structure of the three epoxies was based on BADGE. No spectral modification was seen for chemical functions linked to BADGE. However two additional absorption bands were seen following contact between chlorine and chlorine...
dioxide compared to Evian water only: a band corresponding to a C\(\equiv\)O ketone function and the second one corresponding to an OH alcohol function, both being created by epoxy oxidation in the presence of chlorinating agents. The BADGE chemical structure of the E3 epoxy coating seemed to be more affected than the other two (E1 and E2). A summary of the modifications interpreted from Fourier transform infrared spectroscopy (FTIR) data in the case of E3 is given in Table 1.

The above data distinctly show that the epoxy coatings clearly undergo, all in all, fairly quick oxidation by chlorine and chlorine dioxide given the realistic contact conditions.

Field investigation of epoxy-coated tanks and pipes

In total, 27 real tanks coated with epoxies and ranging in capacities from 60 to 1,500 m\(^3\) were sampled in the west and south suburbs of Paris. The most recent epoxy relining had taken place 1 year before the sampling. Chlorine residuals ranged from 0.04 to 0.5 mg/l. None of these tanks showed detectable levels (<10 ng/l) of bisphenols A and F or chlorinated phenols attributable to bisphenol A oxidation.

Historically, the Geopox GX 014 process developed and initially deployed in the United Kingdom, was certified in France in the 1990s and used in particular by the Lyonnaise des Eaux company to rehabilitate dozens of kilometres of corroded pipes. The first organoleptic problems (musty and pharmacy-type odours and colour) appeared in 2008 in a very restricted geographical area and reappeared on a larger scale in 2011, leading to inspection of around 200 sections of pipe. Bisphenol A and bisphenol F were observed in a significant proportion of the 200 pipes sampled (Table 2) during the period from May to August 2011. 2,4,6-trichlorophenol which was observed on a few samples is a known chlorination by-product from bisphenol A (Yamamoto & Yasuhara 2002), and the precursor of the musty odorant 2,4,6-trichloroanisole. In some cases, the level of bisphenol A exceeds 100 ng/l, a value taken as a reference by the French health authorities. Some of the other phenols and halophenols investigated, in particular isopropylphenol and dichlorophenols were investigated as

**Table 1 | Differences observed between E3 epoxy resin’s FTIR spectra according to the different contact conditions**

<table>
<thead>
<tr>
<th>Absorption bands</th>
<th>Chemical links / chemical functions</th>
<th>Modifications of E3 spectra with water - Cl(_2)/Evian water</th>
<th>Modifications of the E3 spectra with water and ClO(_2)/Evian water</th>
</tr>
</thead>
<tbody>
<tr>
<td>880 cm(^{-1})</td>
<td>C – H (aromatic C) on a monosubstituted benzenic nucleus</td>
<td>Appearance of peak</td>
<td></td>
</tr>
<tr>
<td>1,065 cm(^{-1})</td>
<td>C – O (alcohol function with C linked to an aromatic nucleus)</td>
<td>Appearance of peak</td>
<td></td>
</tr>
<tr>
<td>Wide band between 1,350 and 1,470 cm(^{-1})</td>
<td>C – H (methyl function (CH(_3)) at 1,350 cm(^{-1}) C-C aromatic chain at 1,470 cm(^{-1}))</td>
<td>Appearance of a wide band indicating the emphasised presence of these functions and an eventual restructuring around the aromatic nucleus</td>
<td></td>
</tr>
<tr>
<td>1,650 cm(^{-1})</td>
<td>C = O/ketone function</td>
<td>Appearance of peak – epoxy oxidation</td>
<td>Appearance of peak – epoxy oxidation</td>
</tr>
<tr>
<td>1,730 cm(^{-1})</td>
<td>C = O/ester function</td>
<td>Appearance of peak – epoxy oxidation</td>
<td>Appearance of peak – epoxy oxidation</td>
</tr>
</tbody>
</table>
they were detected in the same area during the first incident in 2008, but were not detected.

By contrast with laboratory leaching tests of recent epoxies, bisphenol F was always present and often more concentrated than bisphenol A in these field samples. It is not known whether this difference reflects a difference in composition between old and new epoxies, or an effect of aging. It is not understood either why the ratio between bisphenol A and bisphenol F is varying so widely (see Table 2). This could result from a complex combination between their leaching, and their respective reactions with chlorine and chlorine dioxide. It was not possible to establish a statistical link between the pipe characteristics (rehabilitation date and diameter) or the water (flow rate, chlorine residual, temperature, pH) and the bisphenol contents observed. As part of these pipes also showed musty odours caused by 2,4,6-trichloroanisole, and in some extreme cases, a pink colour, it appears that a renewal programme will have to be undertaken.

The difference between rehabilitated tanks and pipes can be explained by several factors including: (1) the higher S/V ratio for pipes; (2) the residence time in a pipe located in a branch can be higher than in a reservoir; and (3) the polymerisation conditions are likely to be much more unfavourable during pipe rehabilitation compared to tank rehabilitation. One technique consists in a compressed air turbine which sprays the coating on the wall, which is then smoothed by a rotating brush system. Paint drying time is relatively short, around 8 hours and air can be incorporated during spraying creating bubbles. With this type of procedure, the mix of both compounds (polymer and hardener) is carried out in situ and it is believed that this mix may not be perfect, leading to poor polymerisation. Furthermore, insofar as the pipe remains buried, pockets of humidity can remain on the walls, constituting a major obstacle to the setting of the epoxy resin.

### CONCLUSIONS

Leaching tests carried out with three types of currently approved epoxy coatings applied under well controlled
conditions indicated generally low but detectable leaching of bisphenol A. None of the systems exhibited Fickian type diffusion of BPA and one of the systems even showed a trend of increasing leaching during the first 5 months of immersion. This seems to imply that official approval tests which are based on a 1 week immersion period might not be adapted to all types of materials and that a verification after 6 months should be envisaged. The observed behaviour of 2,4,6-TCP, a known BPA chlorination by-product, seems to imply that disinfectants penetrate inside the coating and that oxidation reactions do take place within the mass of the polymer.

A change of colour of the test panels indicated a rather quick aging of the coating, which was confirmed by FTIR analysis which showed the formation of carbonyl and alcohol functional groups indicative of oxidation reactions.

Field sampling of 27 real tanks tends to indicate that BPA leaching should not represent a problem for full-scale tanks with a volume higher than 100 m$^3$ and laid according to manufacturers instructions (curing T, curing time and humidity). By contrast, examination of about 200 pipe sections in an area where organoleptic disorders (medicinal and musty taste, red colour) had been observed since 2008, indicated a significant detection frequency of bisphenol A and F with maximum values around 1 $\mu$g/l. Therefore, rehabilitation of pipes with epoxy linings should be discontinued. The pipes investigated were all located in areas disinfected partially or in totality with chlorine dioxide and it is possible, by analogy with previous observations with polyethylene, that this disinfectant had accelerated the aging of epoxy.

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