BPA-free strategies for relining drinking water pipes

Context

The relining[1] or curing-in-place[2] of drinking water pipes often use an epoxy resin whose principal monomer is Bisphenol A Diglycidyl Ether (BADGE), which can release BPA. These processes involve inserting a leak-proof coating inside the pipe, which makes it possible to avoid replacing damaged water pipes with new ones and thus keeps costs down.

While, to date, there has been little analysis of the chemical composition of the water from relined pipes, migration of BPA and BADGE into the water has already been reported in several cases where the epoxy resin was not properly mixed or did not have sufficient time to dry.

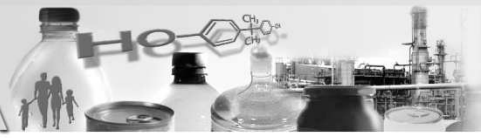
In 2011, various NGOs (Réseau Environnement Santé, Chemsec International Chemical Secretariat and Women in Europe for a Common Future – WECF) raised the question of the rehabilitation of drinking water supply pipes (the coating of tanks and pipes) using the technique known as "relining", which could cause Bisphenol A (BPA) to be washed into drinking water.

Wash-out of Bisphenol A from epoxy resin

Epoxy resins are formed by the polymerisation of Bisphenol A (BPA) and epichlorohydrin. The pre-polymer thus obtained (bisphenol diglycidyl ether) is mixed with a hardener in situ during installation. However, if the proportions of the two components (the pre-polymer and the hardener) are wrong, or if the time necessary for polymerisation of the resin is not respected, hardening will be imperfect and the epoxy may release Bisphenol A and other additives. The time necessary for hardening of the resin may be reduced by increasing the temperature, by injecting hot water or steam, or by exposing it to UV radiation. In Germany (UBA, 2010a) (UBA, 2010b), it has been shown that the quantity of BPA in the water increases with the temperature of the pipes or the water. Several reports indicate BPA concentrations of over 30 µg/L (micrograms per litre) in water heated to 70°C. BPA levels of up to 280 µg/L have been measured in hot water pipes following a relining operation that was not performed properly. These levels were well above the German regulatory threshold of 30 µg/ L. In 2002, Roméro et al., and Bae et al., published two articles almost simultaneously on the migration of Bisphenol A from epoxy resins authorised for use with drinking water. Romero et al set up a controlled migration test in Spain, soaking metal plates or cement slabs (around 100 cm2) covered in epoxy resins in one litre of ultra-pure water for 5 days at 40-45 °C.

[1] Relining: Injection of a resin solution until the defect observed is fully sealed.

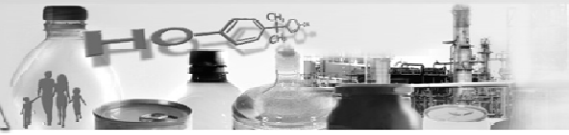
[2] Curing-in-place: Curing-in-place involves inserting a soft envelope soaked with hardening resin inside a damaged collecting sewer, without leaving any annular space.



The water in contact was then extracted using a liquid-liquid extraction method (giving a yield of 97-101% for Bisphenol A) and the extracts were measured by GC/MS, with separation in the non-polar DBS phase. Bisphenol A was identified in all the samples from metal plates (3 different epoxy resins) and one of the two cement samples, with a maximum concentration of 0.02 to 0.03 µg/cm2.
A study conducted by the CIRSEE (International Research Centre on Water and the Environment) in November 2011 studied the behaviour of new epoxy resins in controlled laboratory conditions, as well as conducting measurement campaigns on water tanks and pipes that had been rehabilitated with epoxy resins since the 1990s. The results of this study are detailed below:

1°) For the new epoxy coatings tested in the laboratory, the first conclusion that emerges is that, in realistic implementation conditions (water temperature, residual disinfectant, etc.), bisphenol release is around 10 to 30 ng/L during the first week of immersion. These values seem to be maintained for the next six months, and can reach 180 ng/L after 5 months, depending on the epoxy resin used.
Two observations tend to indicate fairly rapid ageing of the epoxy resins in contact with chlorinated water. First of all, there is quite distinct yellowing of the initially light-coloured epoxy resins after two months of immersion. This yellowing is distinct for epoxy resins in contact with chlorine dioxide and is observable to a lesser degree in the presence of chlorine. No trace of BPA is detected after 4 months of immersion of the epoxy resins in chlorinated water. Only the release of a by-product of BPA, 2,4,6-trichlorophenol (TCP) was observed, which indicates that the disinfectant reacts with the BPA, probably in the resin itself. We also noted, after the end of the chlorine dioxide injection, that for the two epoxy resins that released the least BPA, the BPA release rate was higher than that observed when there had been no exposure to the disinfectant. This could be due to chemical damage to the epoxy resins caused by the chlorinated disinfectants.

2°) As regards the measurement campaign, conducted by the CIRSEE in 2011 on 27 drinking water tanks in the Paris region that had been rehabilitated with epoxy resins between the 1980s and 2010, analysis of the water did not reveal the presence of any Bisphenol A or 2,4,6-trichlorophenol (TCP). This study also showed that, according to measurements conducted in the pipelines rehabilitated from the early 1990s until quite recently, a majority of such pipes release Bisphenol F and around a quarter release Bisphenol A at levels that may exceed 1 µg/L in the water.
Pending the replacement of the pipes already in place, the authors of the study recommend maintaining sufficient residual disinfectant to destroy the Bisphenol A and its primary chlorination by-products (chloro-bisphenols in the case of chlorine). A residual content of 0.15 mg/L of dioxide and 0.2-0.25 mg/L of chlorine should suffice, they say.



Replacement products/Sanitary Conformity Certificates

PIPES FOR DRINKING WATER

The use of organic materials in contact with water destined for human consumption is subject to regulatory provisions (see 4) and must obtain:

- **a Sanitary Conformity Certificate (ACS),** issued by one of the laboratories accredited by the Minister of Health, which constitutes proof of compliance with regulatory requirements. *The Sanitary Conformity Certificate (Attestation de Conformité Sanitaire or ACS) enables assessment of the suitability of a material or object for use in contact with water destined for human consumption, in light of the regulatory provisions. The conditions for the issuance of ACS certification for organic materials and objects are specified in the circulars of 12 April 1999, 27 April 2000 and 21 August 2006, cited above.*

- **evidence of the compliance of the chemical formula with positive lists of reference chemical substances (CLPs)**, issued by one of the laboratories accredited by the Minister of Health. This evidence must demonstrate compliance with the regulatory provisions for seals less than 63 mm in diameter, glues, greases and lubricants (see circular of 20 April 2000), organic additives and admixtures for cement, and ready-to-use cement-based industrial coatings applied in situ.

The list of organic materials coming into contact with water destined for human consumption with:
- a Sanitary Conformity Certificate (ACS);
- evidence of compliance with the positive lists (CLPs);
is published regularly by the Directorate-General for Health (last updated: 31/12/2011).

The validity period of a Sanitary Conformity Certificate (ACS) or of proof of compliance with the positive lists (CLPs) for an organic material is set at five years. The validity period may, however, be extended to 10 years for resins used in the manufacture of extruded polyethylene tubes, in the conditions set out in Appendix B to the circular of 27 April 2000.

There exist BPA-free materials with ACS certification that can be used in the relining process: materials made from polyester/polyurethane, for instance.

AUTHORISED COATINGS

The breakdown of authorised products (products with an ACS) by category is as follows (31/12/2011):
Epoxy resin: 70 (48%)
Cement with admixture: 12 (8%)
Polyurethane: 5 (3%)
Composite coatings: 24 (16%)
Other coatings: 36 (25%)
The "other coatings" category includes materials made from Rilsan (a polyamide derived from castor oil), PVC membranes, membranes made of polypropylene, Ebonite and other materials whose nature is not specified (only the commercial name is indicated).
We can see that epoxy resins account for around 50% of approved materials.

Polyurethane

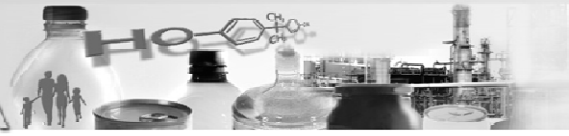
This resin (100% polyurethane) is preferable in terms of water quality. This is due both to a very quick hardening time and to the absence of solvent. The absence of the partially-soluble components and strength-increasing admixtures (BPA) which are present in epoxy resins avoids problems concerning effects on the taste and smell of the water. Furthermore, the quick hardening time, in comparison to epoxy resins, reduces the probability of a rehabilitated pipe being returned to service before the resin is totally dry and thus releasing volatile compounds, which have a negative impact on water quality.

Cement-based coating

A Ministerial Order concerning evidence of the sanitary conformity of materials and finished products made from cementing materials (concretes, mortars) that come into contact with water destined for human consumption is currently being drawn up and will soon update the conditions for assessing the sanitary conformity of these materials and products. Pending the finalisation of said draft Order, the opinion of 24 February 2012 on the conditions for initial market release of materials and objects made from cement that enter into contact with water destined for human consumption in water production, treatment and distribution systems, published in the Official Journal of the French Republic n 0047 of 24 February 2012, specifies the nature of the evidence of sanitary conformity expected for cement-based materials. With regard to organic additives and admixtures designed to be incorporated in cement-based products, and ready-to-use cement-based industrial products for in situ application, obtaining a certificate of compliance with the positive lists (CLPs) issued by one of the laboratories accredited by the Minister of Health, in application of Article R*. 1321-52, constitutes sufficient evidence of compliance with the requirements of the Order of 29 May 1997, as amended. This certificate certifies that the substances used in the manufacture of the materials comply with the requirements in force concerning use in contact with water destined for human consumption. The issuance of this certificate is not contingent upon the performance of water migration tests. According to telephone conversations with the Suez company, cement is currently used to rehabilitate water networks instead of BPA epoxy resins.

Silicone resins

No silicone-based products approved in France (with an ACS) for the rehabilitation of pipes have been identified, but there are products with an ACS whose nature is not specified and which could be silicone-based. Technical tests performed in Sweden have shown that silicone polymers could be used to replace epoxy resins. This new material shares most of the properties of epoxy resins (it hardens at ambient temperature, it has the same "mechanical" properties, etc.). However, the cost of this material is much higher than that of epoxy resins, even if this cost is reduced by simplification of the hardening process. Moreover, this new material is registered in the Swedish BASTA base, (Byggvarubedömningen and SundaHus) a base identifying the materials that are not harmful to human health or the environment and can therefore be used in the construction sector.



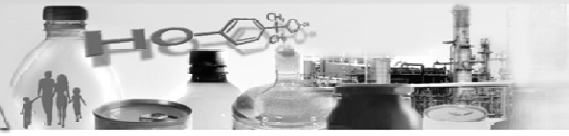
WASTEWATER PIPES

The products must comply with the technical specifications set out in the valid Technical Opinions. Unlike in the regulations for drinking water, no tests are required on the migration of substances into the water.
Based on the Technical Documents for Application drafted by the CSTB (the French Scientific and Technical Centre for Building), the resins used in the rehabilitation of wastewater pipes (other than epoxy resins with BPA) are as follows:
- Polyester with styrene
-Polyester without styrene
-Vinylester.

Foreign regulations

Many countries have set up a system requiring accreditation of materials for use in contact with water destined for human consumption. In these countries, the majority of authorised products are epoxy resins.
In Germany, the rehabilitation of pipes is covered by the "Guideline for Sanitary Assessment of Organic Coatings in Contact with Drinking Water" (30/11/2010), which sets the thresholds for "migration" of BPA into drinking water at 30 µg/L, and 450 µg/L for BADGE. The German Federal Environment Agency (UBA) encourages companies to certify the substances and processes used in relining (analysis method: DIN EN 13130-13:2005). However, epoxy resins continue to be permitted.

In the United Kingdom, the body in charge of monitoring drinking water (the Drinking Water Inspectorate - DWI) lists the products approved for use in the public water system, which must be applied by accredited contractors. The list of approved products for rehabilitating pipes is more restricted in France. It includes epoxy resins and polyurethane-based coatings.
In Sweden, the rehabilitation of pipes is not subject to any regulation. To rectify this situation, the Swedish Construction Federation has strongly advised against the use of epoxy plastic materials, and asked that regulation be introduced on relining.
In the USA, materials in contact with water destined for human consumption must be approved according to Standard NSF/ANSI 61: "Drinking Water System Components" (1988).
In the Netherlands, materials in contact with water used for human consumption are approved by the KWR (Kiwa Water Cycle Research Institute) along similar lines to the French system.



Future outlook

Several dozen epoxy-resin-based coatings are currently on the list of water-contact materials that have received a Sanitary Conformity Certificate (ACS): there are 70 epoxy-resin-based coatings on this list, representing 50% of all certified substances in this field.

The rare publications that exist on the migration of BPA into water from epoxy resins suggest that the phenomenon remains limited and that the quantities ingested through water are considerably lower than those ingested through food (ANSES 2008). However, due to the fact that these migration results were obtained in the laboratory (in very controlled conditions), it will be incumbent upon water distributors, among others, to check and complete these data, through a comparative study of the behaviour of different epoxy resins in the presence of chlorine and chlorine dioxide.

Studying water in contact with epoxy resins of different ages would make it possible to provide answers concerning the long-term diffusion of BPA.

In this context, the Swedish government has asked the Swedish Chemicals Agency, the National Housing, Construction and Planning Council, and the National Food Agency to check whether Bisphenol A is released into drinking water from pipes rehabilitated using the relining technique. This study began in January 2013.

While BPA migration is, above all, of concern in drinking water pipelines, where it could contaminate water consumed by human beings, its presence in the lining of wastewater collectors is also problematic, as it increases the quantity of BPA to be treated at treatment plants. Alternatives for relining exist, however: BPA-free polyester- and polyurethane-based materials, and possibly silicone resins. However, the chemical composition of these BPA-free alternatives still has to be evaluated.

References

Bae, B., Jeong, J., Lee, S. (2002) The quantification and characterization of endocrine disrupter bisphenol-A leaching from epoxy resin. *Water Science and Technology*. **46**, 381-387.

ChemSec 2011 « Bisphenol A in relining of water pipes" www.chemsec.org.

CIRSEE (Suez Environnement) « Risques Sanitaire et organoleptiques associés au relargage de bisphenol A par des revêtements epoxy dans les réseaux de distribution (étude bibliographique) décembre 2010.

CIRSEE (Suez Environnement) : « Risques Sanitaire et organoleptiques associés aux résines epoxy (partie expérimentale) »novembre 2011.

Direction Générale de la Santé (DGS) 31 Décembre 2011 : Liste des matériaux et objets organiques entrant au contact d'eau destinée à la consommation humaine disposant :
- D'une attestation de conformité (ACS),
- D'une preuve de conformité aux listes positives (CLP),
- D'un CAS pour les fibres ensimés.

Kang, J.H. and Kondo, F. 2002. Effects of bacterial counts and temperature on the biodegradation of bisphenol A in river water. Chemosphere 49: 493-498.

Leaching of Bisphenol A and F from new and old epoxy coatings: Laboratory and Field Studies : Auguste L Bruchet, ph.D CIRSEE Le Pecq, FRANCE 2012.

Romero.J, Ventura.F, Gomez.M : "Characterization of paint sample used in drinking water reservoirs : identification of endocrine disruptor compounds" Journal of Chromatographic Science, 40,191-197 2002.

UBA "Guideline for Sanitary Assessment of Organic Coatings in contact with drinking water (coating guideline)" 30/11/2010.
http://www.umweltbundesamt.de/wasser-e/themen/downloads/trinkwasser/beschichtungsleitlinie.pdf

UBA. (2010) :" Bisphenol A. An industrial chemical with adverse effects.

U.S. EPA and U.S. Department of Defense Toxicology and Risk Assessment Conference (TRAC) 2007 Cincinnati, Ohio, "Derivation of BPA oral reference dose (RfD) and drinking water equivalent concentration".

Water Research Foundation and Drinking Water Inspectorate : Impacts of Lining Materials on Water Quality 2010 UK.

Agence française de sécurité sanitaire des aliments , Avis du 21/11/2008 relatif à l'évaluation des expositions et des risques sanitaires liés au bisphénol A dans l'eau destinée à la consommation humaine.

List of companies and organizations contacted

CSTB : Service Hydraulique et Equipements Sanitaires Division Canalisations et Accessoires

Agence de l'Eau Seine Normandie (AESN)

Société TELEREP (Véolia) : Réhabilitation des réseaux d'assainissement

Bureau de Normalisation des Plastiques et de la Plasturgie (BNPP)

Suez Environnement