Lead removal from drinking water – development and validation of point-of-use treatment devices

R. Sublet*, A. Boireau**, V.X. Yang***, M.-O. Simonnot**** and C. Autugelle*****

* Vivendi Water – Anjou Recherche, chemin de la Digue, BP76, F-78603 Maisons-Laffitte, France

** Vivendi Water – Générale des Eaux – Direction Technique, 18 boulevard Malesherbes, F-75008 Paris, France (E-mail: *alain.boireau@generale-des-eaux.net*)

*** Vivendi Water – US Filter Plymouth Products, 502 Indiana Avenue, Sheboygan, WI 53081, USA

**** Laboratoire des Sciences du Génie Chimique (CNRS), 1 rue Grandville, BP451, F-54001 Nancy

***** Laboratoire d'Hygiène et de Recherche en Santé Publique, 11 bis rue Gabriel Peri, BP288, F-54515 Vandoeuvre-les-Nancy

Abstract Two lead removal water filters were developed to lower lead levels in drinking water below 10 µg.L^{-1} in order to meet the new regulation given by the European Directive 98–83, applicable in December 2013. An appropriate adsorbent was selected through a stringent research program among a wide range of media, and is composed of a synthetic zeolite and an activated carbon. Two prototypes were developed: the first is a faucet-mounted filter which contains a fixed bed of the adsorbent and a hollow fiber bundle, while the second is an under-sink cartridge made of a porous extruded block of carbon and adsorbent. Both are able to treat at least 1,000 litres of any water containing on average 100 to 150 µg Pb.L^{-1}, by lowering the lead concentration below 10 µg.L^{-1}. Once their safety considerations were addressed by an independent laboratory according to the French Ministry of Health recommendations, 20 prototypes were installed at consumers' taps in northeastern France. Their performance in terms of lead removal, HPC control and bad taste and odor reduction was followed for 6 months. This field testing program resulted in the validation of both prototypes which meet the new French Ministry of Health recommendations and assures that the filtered water is fully ED 98–83 compliant. Their commercialization will be launched first in France in middle 2002.

Keywords Drinking water; filter; lead removal; point-of-use

Introduction

Following the World Health Organization recommendations (1993), a new European Directive 98–83 lowers the lead parametric value in drinking waters from currently 50 to 10 µg.L^{-1} in December 2013. Though water coming from treatment facilities does not contain lead, contamination can occur when the water flows through lead service pipes and domestic plumbing. The degree of contamination depends on the pipe length and material, and on the water quality (Randon, 1996).

Two lead removal systems for adaptation to kitchen taps were developed and tested. These will be offered to concerned customers as an economical solution until replacement of their lead pipes can be completed.

This project, endorsed by French Ministries (Research and Habitation), was carried out thanks to a strong synergy between teams of differing interests: the research part was performed by the Laboratory of Chemical Engineering Sciences (CNRS). The Laboratory of Hygiene and Public Health Research participated to determine the safety of the devices, whereas Vivendi Water (Generale des Eaux and US Filter) was responsible for the field testing program, which included the design, construction, installation and sampling of the products.

These devices were designed to treat about 1000 litres of a water containing on average 100–150 µg Pb.L^{-1}. Their efficiency to lower the lead concentration below 10 µg.L^{-1} was proved regardless of the water quality.

209

A two-stage filtration system removes first dissolved lead by use of a selective adsorbent, while metallic particles released from the pipes and other precipitates are physically trapped by a 0.45 µm filtration system.

Our paper reports the results of this study which were obtained through coordination of a three stage procedure:

1. selection of adsorbents, making of prototypes and validation of their performances on the main kinds of water that can be usually found in France;
2. testing of the prototypes' safety guided by an official test procedure requested by the French Ministry of Health and developed by a workgroup of the French Public Hygiene Upper Council;
3. testing of prototypes at consumers' taps during 6 months in northeastern France.

This study led to the development and validation of two kinds of devices for use on common French waters:

- the first is a faucet-mounted filter, easy to install and operate. It contains a fixed bed of zeolite coated on a granular activated carbon, and a hollow fiber bundle.
- the second model is an under-sink system, containing a cartridge made of a porous extruded block of powdered activated carbon and zeolite.

Selection of an appropriate adsorbent

The selection process began by focusing on lead speciation in drinking waters. Indeed, Luo and Hong (1997) have studied the dissolution process of lead pipes, and gave the explanation illustrated by the scheme in Figure 1. Many authors have widely studied lead speciation as a function of the water composition, and showed that once lead is dissolved, it can form ion pairs, organic complexes, organic chelates, adsorb itself onto colloids and solids, or finally precipitate with carbonates. The repartition of the different species strongly depends on the water composition, especially pH and alkalinity (Harrison and Laxen, 1980; Schock, 1980; Hunt and Creasey, 1980; Sheiham and Jackson, 1980). At the same time, pure metallic particles of lead can be eroded from the pipes.

The most important thing to remember is that in drinking waters lead ion, Pb^{2+}, is in the minority, and the higher the pH and alkalinity, the more Pb is combined with other ligands, as listed in Figure 1. This list also points out that the size of some species exceeds 0.45 µm, indicating that they are easy to remove by simple mechanical filtration.
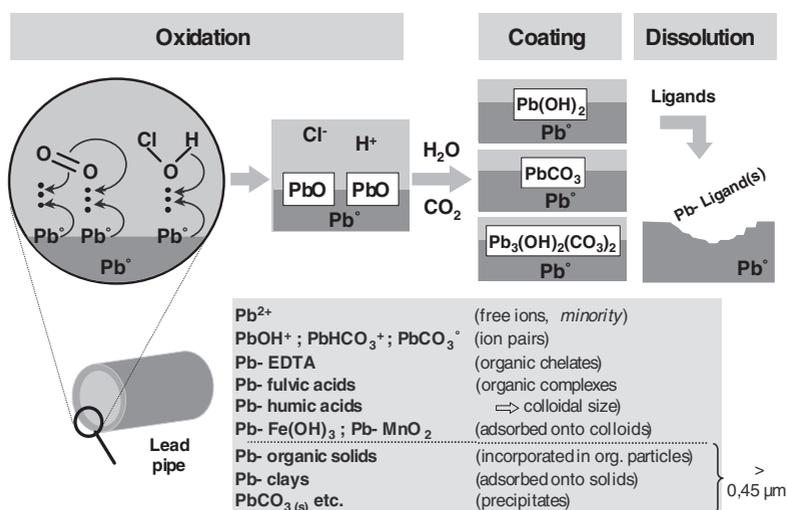

Figure 1 Contamination of drinking waters through dissolution of lead pipes. Luo and Hong (1997)

Taking into account lead speciation is therefore very important for finding an adsorbent capable of retaining all lead species. The results of a literature survey allowed us to identify five classes of adsorbents able to retain lead: natural and synthetic zeolites (Kesraoui-Ouki *et al.*, 1993; Ahmed *et al.*, 1998), metallic oxides (Prigent *et al.*, 1999; Petrangeli Papini *et al.*, 1999), activated carbons (Kuennen *et al.*, 1992), ion exchange resins (Arts *et al.*, 1985) and various chelating agents (Kim and Lee, 1999). This is of course a non-exhaustive list of all past works that have been done around this issue, but most of these research works are not directly applicable to our study because they were almost all done with industrial waste-waters, whose pH is usually acidic (or can be adjusted). In such conditions, lead is in its pure cationic form (Pb^{2+}) and easy to remove.

To select an adsorbent able to withhold all species of lead in very short contact time conditions, a four-step procedure was performed:

1. Batch experiments were carried out first to classify ten media chosen from the five classes of adsorbents listed above (see Table 1) as a function of their equilibrium lead retention capacity for an inlet lead solution concentration of 100 μg Pb.L^{-1}. The following method was employed to plot sorption isotherms:

   0.1 g of medium was placed in 100 mL of Nancy municipal tap water (pH 7.5, hardness 120 ppm $CaCO_3$, alkalinity 60 ppm $CaCO_3$) spiked with a lead nitrate salt at different initial concentrations (1 to 100 mg Pb.L^{-1}). After 24 hours of stirring, the solution was filtered at 0.45 μm and the remaining equilibrium concentration was analysed by ICP-MS. Then, the isotherm curves were constructed by plotting the weight of lead adsorbed per unit volume of solid versus equilibrium lead concentration in solution.

2. Five granular solids (indicated by * in Table 1) were thus selected, placed in 10 mL micro columns and flushed with the Nancy tap water spiked on average at 120 μg Pb.L^{-1}, at a low flow rate (1 mL.min^{-1}). Pure synthetic zeolites and MnO_2 were not tested because of their very small particle size (varying between 1 and 50 μm). This dynamic approach was used to obtain the beginning of the lead breakthrough curve, with sufficient contact time (5 minutes). Media, such as clinoptilolite and the resin, that showed an instantaneous leakage (respectively 20 and 50 μg Pb.L^{-1}) were eliminated.

3. Existing filters chosen from within Vivendi Water's available products were used as prototypes. The three candidate media (ZAC, Chabazite and Mn sand) were tested in these prototypes (see Figure 2 (a) and (b)) to assess mass transfer limitations when placed in real conditions (flow rate of 2 L.min^{-1}). Both devices were flushed by 300 L cycles of the same water (Nancy, 120 μg Pb.L^{-1}). Chabazite presented high mass transfer limitations whereas ZAC and Mn sand filters produced a water containing no more than 4 μg Pb.L^{-1}.

Table 1 Selection of potential lead adsorbents. *adsorbents selected for micro columns experiments

| Name	Family	q (mg Pb/mL media)
SZ 2	synthetic zeolite	100
SZ 1	synthetic zeolite	40
ZAC*	GAC coated with the ZS 1 synthetic zeolite	18
Clinoptilolite*	natural zeolite	15
Chabazite*	natural zeolite	13
R-Ca^{2+} *	weakly acidic cationic exchange resin	10
Mn sand*	natural manganese oxide sand	3
MnO$_2$	synthetic manganese oxide	0.1
GAC*	high-performance powdered activated carbon	< 0.1
CP	cellulose powder	< 0.1
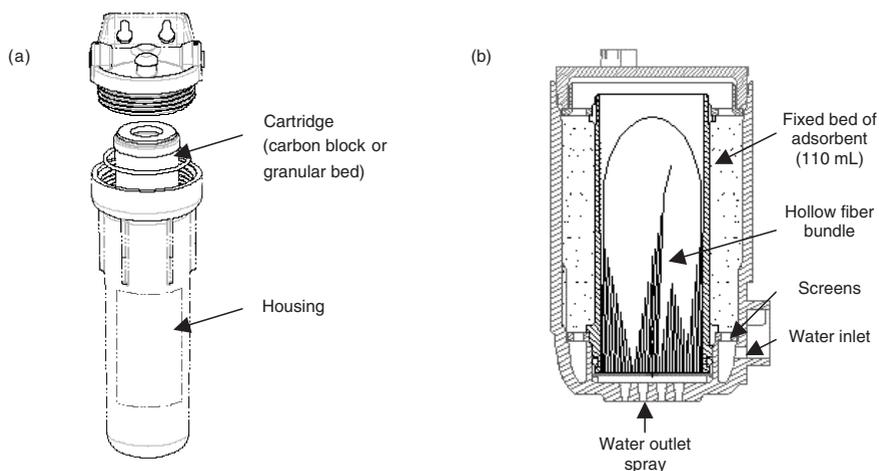
Figure 2 (a) Under sink filter prototype; (b) faucet filter prototype

4. Both efficient media were then tested with four different kinds of water (from soft to hard waters, with pH between 7 and 8), as well as with a water spiked with phosphates (1 mg P.L^{-1}) and their performances were validated.

In addition to these four stages, three prototypes were selected:

- a faucet filter with ZAC as adsorbent,
- an under-sink filter with a cartridge filled with granular Mn sand,
- an under-sink filter with a carbon block cartridge (extruded block of activated carbon and zeolite).

The faucet filter with Mn sand has been abandoned because it was too heavy to be supported by faucets (density of Mn sand = 4 × density of ZAC).

Sanitary safety of the devices

Testing the safety of such devices is very important to ensure that the water produced meets the drinking water regulation. To regulate these Point-of-Use devices, an official test (circular DGS VS4 99-360, 1999) has been requested by the Ministry of Health and elaborated by a workgroup of the French Public Hygiene Upper Council. This testing procedure aims at checking the whole drinking water quality parameters imposed by the European Directive. It comprises 3 stages.

Stage 1: This first stage consists of examining the instructions for use that are included in the package (to check if the information is understandable for the customer and correct), and also checking the chemical composition of all the materials of the whole device that are in contact with the water. All the molecules that compose these materials of construction must be approved for the contact with drinking water and therefore must belong to the latest European updated positive list of materials in contact with food and drinking water.

Stage 2: The aim is to verify that there is no migration of any micropollutant from the device into the filtered water at the installation of the device. The test is carried out with 2 litres of a fairly mineralized water (for instance EVIAN water is used as a reference) chlorinated at 1 ± 0.2 mg/l free Cl.

Stage 3: This last stage aims to check the safety on a complete life cycle of a cartridge (beginning, middle, end). The micropollutants sought here are the same as in Stage 2, but HPC growth monitoring is added to verify that the water keeps a bacteriological quality compatible with an alimentary use. All these tests are done at different steps of the device's

life, in normal use conditions. The tests are performed with the public network water that feeds the laboratory which obviously must meet the French regulations.

To place the water in the conditions of a possible reduction of nitrate (NO_3) into nitrite (NO_2) and/or the possible effect of the presence of organic compounds (measured by TOC), the test water must contain 40 to 50 mg NO_3/l and have a TOC ≥ 2 mg C/l. If the public water does not meet these criteria, it must be spiked with a concentrated solution of a nitrate salt and with a concentrated solution of organic compounds, such as fulvic acids.

To achieve this test, two devices (for duplicate results) are installed on a test stand that allows the control of the flow rate, as well as the programming of the flow between the different sampling series. A third and similar stream is used without a filter as a blank sample, to check a possible contamination of the apparatus. The aim is to simulate the normal functioning of the filter by on/off cycles (3 cycles 1 hour on/ 4 hours off), during at least 10 days, at a maximum flowrate of 300 L/hour. Samples are taken three times:

1. in the first days, for a filtered water volume equal to 10% of the maximum capacity;
2. when the cartridge has reached its half-life and after 60 hours of stagnation;
3. at the end of the cartridge's life.

As each sample is taken 3 times a day, the geometric mean is calculated and the results of the two filtered waters are compared to the blank one. The filters tested so far are compliant with the acceptability criteria of stages 2 and 3, and also with stage 1 requirements.

Field testing program

These three kinds of device were installed at customers' taps in northeastern France, on five different kinds of waters (see Table 2), and their behavior was followed during the 6 month life of a cartridge. The 20 selected clients covered a wide range of families (young to aged couples, with or without children) and of plumbing (service pipes from 2 to 15 meters, with 1 to 30 meters domestic plumbings made of 100% copper, or 100% lead, or copper/lead alternately).

Several parameters were monitored at the kitchen's tap during the whole tests, downstream as well as upstream of the filters.

- Pb concentration. A three sampling method was used: the first flush (1 L), taken immediately at the arrival at the customer's, then the second flush (500 mL) taken after a complete purge of the network, and the third sample taken after a controlled stagnation period of 30 minutes. This last one has been shown by a European study (European Commission, 1999) to be the most representative sampling method of the average amount of lead intake by the consumers, and has become the official one in France.
- taste, assessed by a team of professional water tasters.
- HPC + fecal contamination indicators: coliforms, enterobacter (fecal streptococci), and clostridium (spores of sulfite-reducing bacteria).
- classical parameters such as pH, turbidity, conductivity, hardness, alkalinity, chlorine, and TOC.

Table 2 Kinds of water tested in the field

Municipality	X.	T.	R.	S.	M.
pH	6.5	7.8	7.5	7.4	7.8
Hardness (ppm $CaCO_3$)	5	180	240	280	390
Alkalinity (ppm $CaCO_3$)	15	110	94	265	310
Conductivity (µS/cm)	45	410	510	540	720
Mineralization	Low	Middle	Middle	Middle	High
Other characteristics	aggressive	–	highly sulfated	–	calcifying water

213

During the 6 months, the amount of lead in the non-filtered water varied widely, from 1 to 260 µg Pb.L^{-1}. Figure 3 shows the distribution of lead concentration by type of sampling method.

As supposed, the second flush is the sampling that present the lowest lead concentration (90% < 25 µg.L^{-1}). With the 30 minutes of stagnation method (30 MS), more than 80% of the lead levels exceed 10 µg.L^{-1}. The results of the first flush are similar to the 30 MS ones. It is not a real first flush like the first sample of water taken in the early morning after an entire night of stagnation. The lowest values were obtained in the hardest water. Indeed, such a water (high hardness, pH near 8, and high alkalinity) is not aggressive for lead pipes. The highly soft water with a low pH induced high amounts of lead even with very small lead pipes (2 m), greater than 50 µg.L^{-1} (30MS samplings).

In the filtered water, 100% of the samples contained less than 10 µg Pb.L^{-1}, and most of the concentrations were below 2 µg.L^{-1}.

The professional water tasters as well as the customers found a welcome and significant improvement in the taste of the filtered water, compared to the tap water which is often criticised for its chlorine taste. Their statements were confirmed by the decreased (more than 50%) levels of chlorine and TOC amounts attributed to the filters. But only the media containing activated carbon reduced bad taste. The Mn sand did not bring any improvement, and was therefore rejected.

Classical parameters such as pH, conductivity, hardness and alkalinity were not affected by the whole filters, whereas turbidity was dropped by the submicron filtration effect of the membranes (for the faucet filter) or the pore size of the carbon block. Copper, iron and most of all heavy metals are also removed.

In France, the regulation specifies that fecal contamination indicators are not tolerated in drinking water. It does not impose any maximum level for Heterotrophic Plate Count. Only a recommendation is advised on a maximum of 100 Colony Forming Units at 22°C and 10 CFU at 36°C. During this testing program, no fecal contamination indicator was found in the filtered water, as well of course as in the tap water. The filters meet the regulation for all the drinking water microbial parameters.
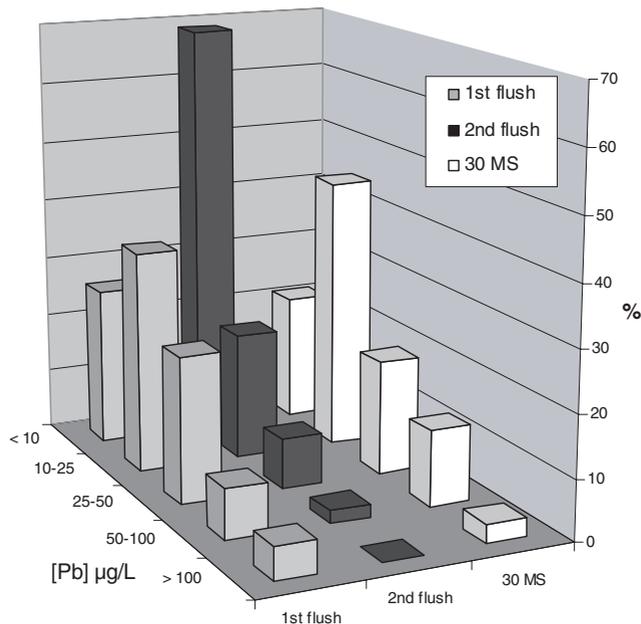

Figure 3 Lead concentrations in non filtered waters

Under-sink devices were proven to be excellent because the HPC 22°C amount was always below 100 CFU, even in the first flush. Faucet filters were significantly colonized: HPC amounts were quite high in the first flush, but quickly decreased after a while. To prevent this bacterial growth, a part of the faucet filters was modified and no HPC growth occurred.

To sum up, the good results obtained in the laboratory were confirmed: the lead removal claim was always reached regardless of the water quality, no release of other contaminants was observed, and the main physical and chemical parameters of the waters were maintained. Moreover the material made of activated carbon and zeolite presents the advantage of reducing bad taste and odor, better than the manganese oxide which was not effective.

Conclusions

The combination of a scientific and technical approach in famous public laboratories involved in chemical engineering (LSGC-CNRS) as well as in testing water treatment devices and material in contact with drinking water (LHRSP), and a practical approach with industries specialized in the construction of Point-of-Use devices (US Filter – Plymouth Products) and in water treatment and distribution (Vivendi Water) has led to a successful result with products which have been validated in the field.

Two lead removal filters were developed, tested and validated for treating water of varying quality that has been contaminated by lead pipes: one faucet filter containing a zeolite coated onto an activated carbon and a membrane bundle, and an under-sink filter whose cartridge is made of the same zeolite and activated carbon but extruded in a solid block. Both are able to remove lead from any kind of water and were designed to treat at least 1,000 litres of water over 6 months. Moreover, these devices have the ability and the advantage to reduce bad taste and odors, as well as copper, iron, and most other heavy metals. It was also shown that such under-sink units contribute a very low HPC growth, and that faucet filters can be modified to improve their bacteriostatic properties.

Acknowledgements

References

Ahmed, S., Chugtai, S. and Keane, M.A. (1998). The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y zeolite. *Separation and Purification Technology*, **13**, 57–64.

Arts, W., Bauch, L. and Bretschneider, H.J. (1985). Eignung von Ionenaus-tauschern in der Ca-form zur Entfernung des echt gelösten Bleianteils im Berliner Haushaltwasser. *Z. Wasser – Abwasser-Forsch.*, **18**, 244–247.

Circulaire DGS VS 4 no 99-360 du 21 juin 1999 relative aux appareils individuels de traitement des eaux destinées à la consommation humaine au robinet. NOR: MESP9930291C.

Curkovic, L., Cerjan-Stefanovic, S. and Filipan, T. (1997). Metal ion exchange by natural and modified zeolites. *Water Research*, **31**(6), 1379–1382.

European Commission (1999). Developing a new protocol for the monitoring of lead in drinking water. Report EUR 19087 EN. Directorate General Science, Research and Development.

Groffman, A., Peterson, S. and Brookins, D. (1992). Removing lead from wastewater using zeolite. *Water Environment and Technology*, pp. 54–59.

Harrison, R.M. and Laxen, D.P.H. (1980). Physicochemical speciation of lead in drinking waters. *Nature*, **80**(286), 791–793.

Hunt, D.T.E. and Creasey, J.D. (1980). The calculation of equilibrium trace metal speciation and solubility in aqueous systems by a computer method with particular reference to lead. Water Research Center – Environmental protection, Technical report TR 151.

Kesraoui-Ouki, S., Cheeseman, C. and Perry, R. (1993). Effects of conditioning and treatment of Chabazite

and Clinoptilolite prior to Lead and Cadmium removal. *Environment & Science Technology*, **27**(6), 1108–1116.

Kim, H.T. and Lee, K. (1999). Application of insoluble cellulose xanthate for the removal of heavy metals from aqueous solutions. *Korean Journal of Chemical Engineering*, **16**(3), 298–302.

Kuennen, R.W., Taylor, R.M., Van Dyke, K. and Groenvelt, K. (1992). Removing lead from drinking water with a Point-of-use Granular Activated Carbon Fixed-bed adsorber. *Journal AWWA*, **82**(4), 91–101.

Luo, Y.-Y. and Hong, A. (1997). Oxidation and dissolution of lead in chlorinated drinking water. *Advances in Environmental Engineering*, **1**(1), 84–97.

Petrangeli Papini, M., Duale Hahie, Y., Troia, B. and Majone, M. (1999). Adsorption of lead at variable pH onto a natural porous medium: modeling of batch and column experiments. *Environmental Science and Technology*, **33**(24), 4457–4464.

Prigent, S., Clanet, F. and Rousseau, M. (1999). Echantillonnage d'eaux de réseau sur un capteur de résine RMnO$_2$ en vue de la détermination du plomb. *Cahiers de l'Association Scientifique Européenne pour l'Eau et la Santé*, **4**(1), 35–41.

Randon, G. (1996). Synthèse du travail collectif réalisé par l'AGHTM sur le plomb dans l'eau de distribution. *Techniques, Sciences et Méthodes*, no 7–8 , 530–535.

Schock, M.R. (1980). Response of lead solubility to dissolved carbonate in drinking water. *J. AWWA*, **72**(12), 695–704.

Sheiham, I. and Jackson, P.J. (1980). Calculation of lead solubility in water. Water Research Center – Environmental protection, Technical report TR 152.

World Health Organisation (1993). *Guidelines for drinking water quality*. 2nd edition, vol. 1, Recommendations World Health Organisation, Geneva.

R. Sublet *et al.*

216