# On-site microwave-assisted pilot-scale plant for treating hazardous waste landfill leachate: a new European LIFE project for asbestos prevention and monitoring

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## ABSTRACT

The acknowledgements of the European Community directive 1999/31/CE have lead to the set up of special landfill areas exclusively dedicated to asbestos, leading to a large increase in the concentration of these carcinogenic fibres in liquid deposits (leachates). The dispersion of such leachates in the environment during some of the treatment process phases (air) or after disposal (water and/or soil) poses a serious environmental and sanitary risk. European regulations currently do not foresee appropriate systems for the elimination of asbestos fibres from such leachates.
The project is carried out within the LIFE European Initiative by researchers of the ISPESL-DIPIA and University of Venice on the Barricalla S.p.A. hazardous waste landfill. The objectives are:

?? To set out analytical methods for quantitative determination of asbestos fibres in leachates (not yet standardised);
?? To determine the level of danger of such leachates;
?? To realise a prototype capable of retaining 99% of the asbestos fibres with dimensions considered being dangerous. This pilot plant will be engineered by Bi.Elle s.r.l.

## KEYWORDS

Asbestos, leachates, microwave digestion, filtration

## INTRODUCTION

Treatment and management of hazardous waste landfill leachates has never been a simple task due to the large variability in composition and low stability with time of such liquids.
A study conducted in 2002 by the Venice University at the Barricalla (Turin, Italy) landfill pointed out the presence of significant amounts of asbestos fibres, certainly related to the massive concentration of asbestos-containing materials (ACM) disposed in this landfill (see Fig.1). Leachates from different cells and lots were sampled and analyzed reporting an average concentration of asbestos fibers between 0.8-1 MFL (million fibres per litre) (1).

Preliminary tests (1) performed at the Barricalla landfill indicated that a 220/25/1 µm sequence of polypropylene filters is required in order to obtain a retention of 99 % of the asbestos fibres in the leachate produced by cells strictly dedicated to ACM, which have typically low contents of organic matter. On the contrary, for leachates produced by non-dedicated cells an extended pre-treatment for reducing organic pollutants is needed in order to successfully filter asbestos fibres. Although the 99/31/CE regulation recommends ACM-dedicated cells, most of the leachates presently treated and most of those that will be treated at least in the next ten years will need a pre-treatment.

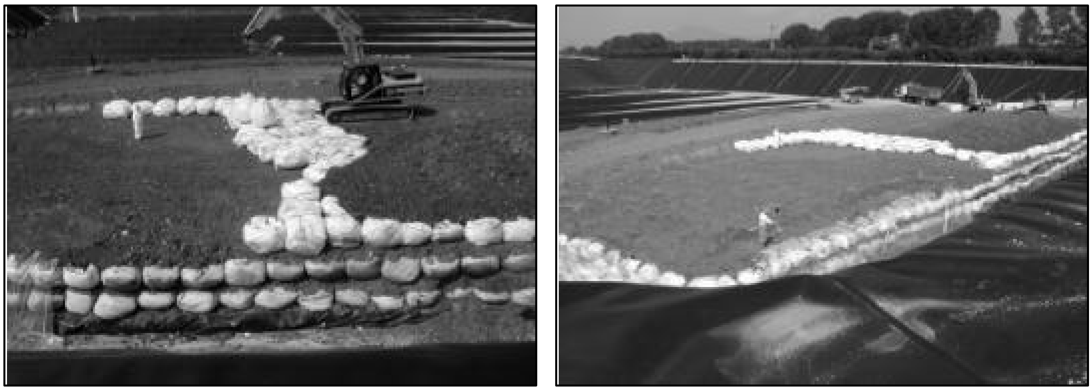

*Fig 1. Disposal of asbestos containing waste at the dedicated cell of the Barricalla landfill.*

As shows in Fig.1, at the asbestos-dedicated cell of the Barricalla hazardous waste landfill each layer of bags is covered with inert material to prevent aerial pollution during the disposing phase. While these precautions should be sufficient to assure workers' safety, the mechanical stresses induced by trucks and compactor moving over the top soil for routine disposal practice could induce the big-bags degradation and breakage phenomena causing the release of more free particles into the soil. Leachates produced by such dedicated cells support this suppositionsince they show a large amount of dispersed asbestos fibers and particles (1) especially during the waste disposing period. To avoid an increasing risk in managing asbestos affected leachates at conventional off-site wastewater treatment plants and to prevent faulty disposal of sludge or hazardous residues, we propose a method for monitoring and filtering asbestos fibers in organic-containing leachates by adopting a microwave-assisted pre-treatment on-site step. A 32 months EU project (Life-Environment), named FALL (Filtering of Asbestos fibers from Leachate of hazardous waste Landfills, ENV/IT/00323) was approved and started on October 2003.

## THE ANALITYCAL METHOD

As for the analytical method, a problem was encountered during SEM analysis of polycarbonate membranes due to the presence of organic matter in the leachate. As shown in Fig 2. the deposition of 50 ml of raw leachate onto a 0.45 µm membrane generates a thick layer of organic compounds embedding all the micrometric particles and fibres and avoiding recognition and counting. Therefore, an oxidation pre-treatment for reducing organics is needed. The microwave assisted closed-vessel acid digestion is preferable to other standard oxidations techniques due to two major advantages:

1) Operations are conducted directly on liquid sample;
2) Reaction time is extremely reduced.

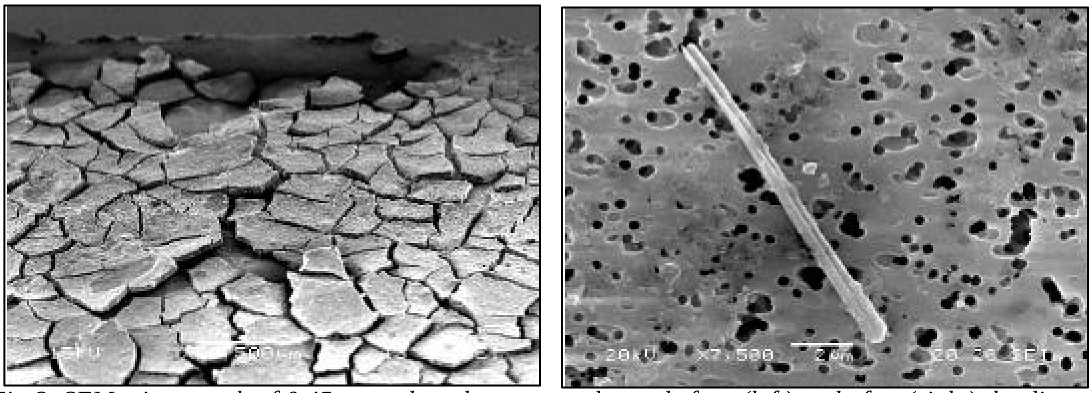

*Fig 2. SEM micrograph of 0.45 um polycarbonate membrane before (left) and after (right) the digestion pre-treatment. Since the organics matter has been digested the asbestos fibers may be identified with EDS analysis and counted.*

However, the amount of organic content in the leachates depends on a large number of variable features, like the amount and frequency of meteorological precipitations, the age of the landfill cell, the type and stabilization degree of the disposed waste. It is therefore impossible to determine a standard pre-treatment which is applicable to any situation.

For leachate with COD values in the range 1000-2000 mg/L we determined a digestion method which uses the microwave workstation CEM Mars5. For higher COD values a dilution step is needed. The operative parameters used by this method are summarized in Table 1.

| | |
|---|---|
| Raw Leachate/vessel (ml) | 25 |
| $H_2SO_4$ 98% /vessel (ml) | 0.5 |
| $H_2O_2$ 35% /vessel (ml) | 4 |
| Max vessel/run (N°) | 14 |
| Leachate/run (Max ml) | 350 |
| Ramp to temp step I (C°/10 min) | 90 |
| Ramp to temp step II (C°/10 min) | 160 |
| Max pressure step I(psi) | 80 |
| Max pressure step II(psi) | 250 |
| Power step I (W ) | 300 |
| Power step II (W ) | 600 |
| Holding time at 90° (min) | 1 |
| Holding time at 160° (min) | 1 |
| Total time (min) | 22 |
| Cool down (min) | 15 |

*Tab.1Operative parameters of the method for the digestion pre-treatment of raw leachate samples.*

The microwave workstation is provided with 14 PFA vessels (100 ml each). Each vessel is provided with a security valve for releasing the gas if the environment reaches the maximum allowed pressure (250 psi). One of the vessels (the monitor vessel) is provided with temperature and pressure detectors interfaced with a personal computer. An typical plot of the reaction parameters during digestion is presented in Fig.3

A program controls the amount of microwave radiation emitted (max 1200W) providing constant heating with time.

If the digestion process has been occurred completely, the treated leachate should be clear and almost colourless. Experimentally, we observed that even a light coloration of the treated leachate produces membranes which are not sufficiently clear for SEM investigation. In this case, it is necessary to increase the $CO_2$ conversion by diminishing the volume of raw leachate per vessel or by using more oxidant reagents. In the latter case, care must be paid in order not to over-pressurize the vessels.

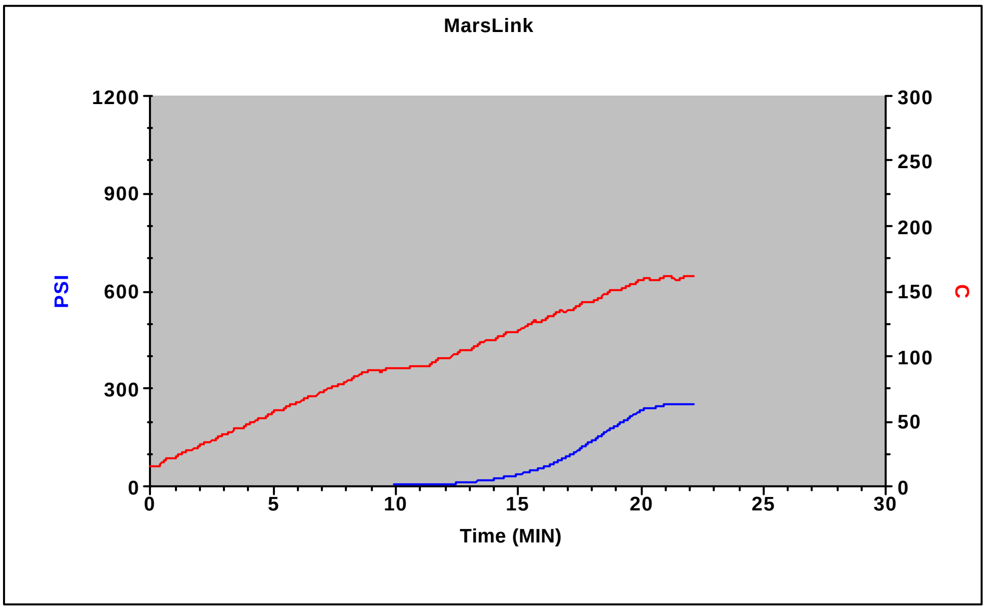


*Fig. 3 Reaction parameters during digetion of raw leachate with the method presented in Tab.1 The complete digestion of 25 ml of raw leachate (COD 1280 mg/L) produces 200 psi (13.6 atm) at 160 °C.*

After such a digestion pre-treatment, samples are filtered on 0.45 µm membranes for SEM or TEM investigation. The volume to be filtered is related to the membrane diameter and to the load of mineral fibers and particles of the leachates. The objective is to produce a filter on which the particles are well distinguished and uniformly distributed minimizing their overlapping. The analytical sensitivity is strictly dependent on the filtered volume, as shown in Tab.2. It not possible to assure an homogeneous deposition using volumes smaller than 50 ml for 47 mm diameter membrane and 10 ml for 25 mm diameter membrane. In this case, a dilution with distilled water is recommended, if a larger sample volume is not available.

| Filtered Volume (ml) 47 mm* diameter | Analytical sensitivity (fibers/liter) | Filtered Volume (ml) 25 mm* diameter | Analytical sensitivity (fibers/liter) |
|---|---|---|---|
| 300 | 3780,00 | 300 | 396,67 |
| 200 | 5670,00 | 200 | 595,00 |
| 150 | 7560,00 | 150 | 793,33 |
| 100 | 11340,00 | 100 | 1190,00 |
| 50 | 22680,00 | 50 | 2380,00 |
| 25 | 45360,00 | 25 | 4760,00 |

*Tab.2 Analytical sensitivity as a function of filtered volumes and membrane diameters. Concentrations are calculated for the case when one fiber is observed over an area of 1mm$^2$.*
**assuming that the effective area of deposition with the filtering system adopted is 199 mm² for 25mm diameter membranes and 1134 mm² for 47 diameter membranes.*

For the aim of this project, routine analysis are carried out by digesting 300 ml of raw leachate and filtering the resultant volume on a 0.45 µm polycarbonate membrane. SEM observation allows morphologic recognition of asbestos fibers and their mineralogical classification with EDS spectrum analysis. Fibers dimensions are measured and reported as “standard” if they comply with Italian regulation (2) (Length >5 µm, Diameter <3 µm and L/D =3:1). As for TEM observation, the diffraction pattern is also useful for determining mineral structure and classification of the fibers. EPA 100.1 and 100.2 regulations describe the technique and prescribe to count all the asbestos fibers with a length > 0.5 µm and an aspect ratio L/D = 5:1 (3).

## LEVEL OF DANGER

The hazardous potential of landfill leachates is roughly predictable since these liquids reflects the composition of the matrix of the waste from which they derive. European regulations are going toward a more strict waste management policy showing major concerns in all the phases of the disposal: leachate disposal as landfill post-closure compulsory activity (30 years) and dedicated cells for special wastes are clear manifestation of this purpose. For these reasons the level of danger of hazardous waste landfill leachate is under investigation as a main objective of the FALL-project.

Danger is strictly dependent on the composition and on the destination of such leachates. If no treatment or disposal is carried out, hazardous waste landfill leachate could be very toxic for environment and humans for its capability of releasing pollutants in air, at the groundwater level or into the soil with clear consequences over all the food-chain. At the same time disposing leachate at inadequate wastewater treatment plant is not correct for the hazard that may be generate during the treatment stages.

Airborne emissions during biological treatment or dewatering and disposing of sludge are possible hazardous operations. Nanoparticles, fibers or volatile organics may enter the environment and be inhaled by on site workers or be winded to the neighbourhood (4). TEM micrographs of membrane deposition of Barricalla hazardous waste landfill leachate are presented as an example in Fig. 4.

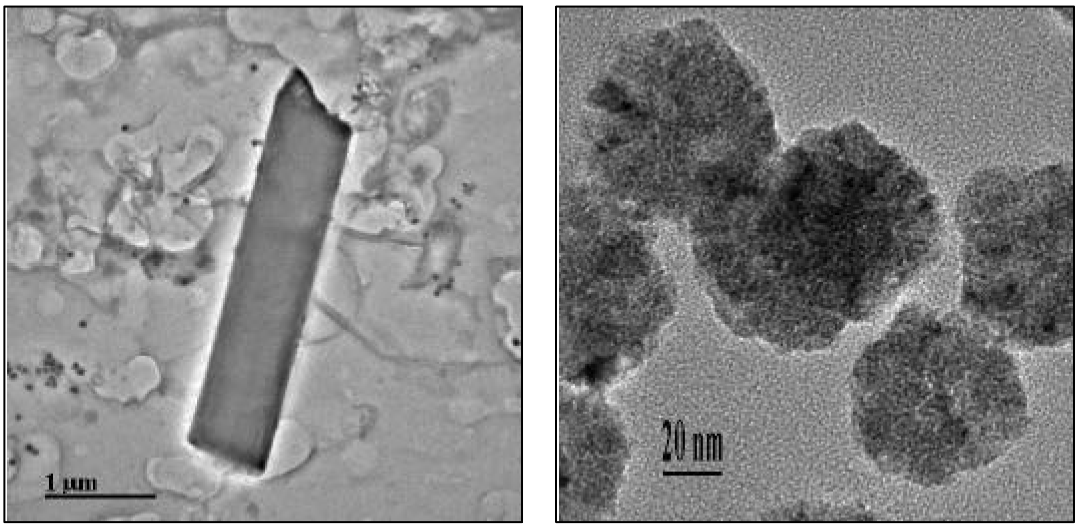


*Fig.4 TEM micrographs of amosite asbestos fiber (left) and tin metallic nanoparticles (right)*

An amosite asbestos fiber with a diameter of 0.8 µm is shown on the left. Fibers of such dimensions are easily passed unobserved when using SEM analysis. However, the dimension of these fibers is even larger than that the one accepted for standard U.S. EPA asbestos determination in water, as mentioned above, and should be counted because of its carcinogenic property.
Many black spots are also recognizable in the same micrograph near the fiber and on the left side. These are magnified and showed on the right micrograph. A large number of these particles have been found all over the grid and have been identified by EDS as metallic tin nanoparticles.
Dimensions, bio-persistence, aerodynamic profile and surface reactivity of the particles are the most important features for determination of hazardousness for the organism due to the possibility of being directly assimilated and not filtered by the natural defence system generating reactive oxygen species (ROS) and causing DNA damage. So, as asbestos, titanium dioxide, metallic nano-particles and carbon nano-fibers are going to be monitored and reported in the analysis that we will conduct over the two years of sampling.

## THE PROTOTYPE

As for the prototype, a scheme of the pilot scale plant for filtering asbestos fibers on landfill sites is presented in Fig.4. It is composed of a 220 µm pre-filter device, acting at the inlet as a screen for the following 100 lt closed tank microwave batch reactor (2x8 kW magnetrons at 2,45 GHz), which is followed by a two-step 25/1-0.5 µm filtration sequence. The reactor is made of AISI-316 stainless steel and designed for operating up to 12 atm and 140°C.

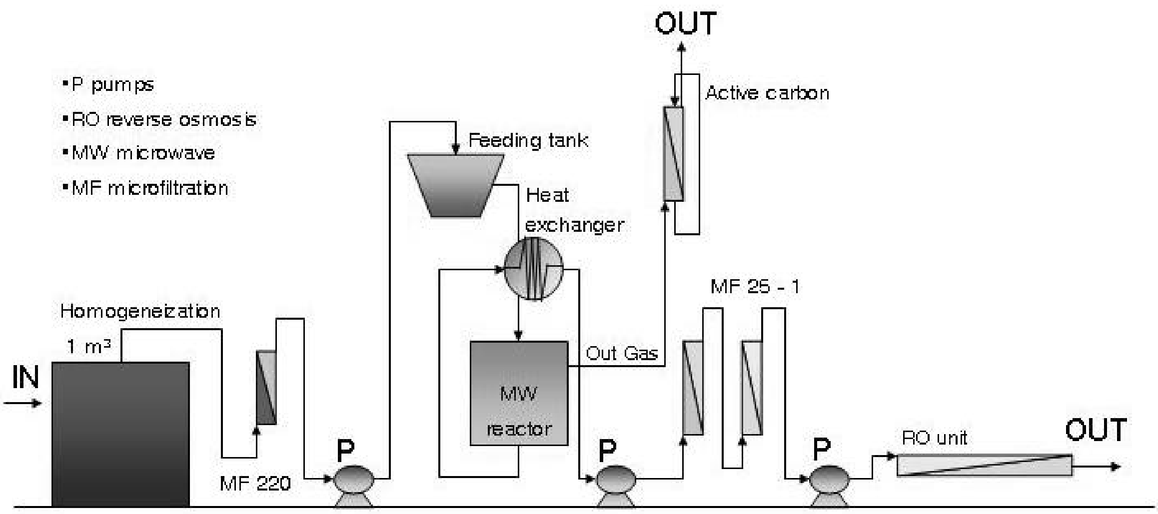


*Fig.5: Pilot-scale plant for the on site pre-treatment of asbestos containing landfill leachate.*

Temperature and pressure may be monitored in real time and a security electro-valve is settled for venting. An active carbon unit has been devised for the out-gas, as well a heating exchanger before the liquid enter the filtration step. Oxidation is provided by supplying an appropriate acid/$H_2O_2$ ratio mixture added to raw leachate and by bringing the solution at ca.120°C with the extremely efficient microwave radiation. We expect to digest a charge of 50 lt. in about 15 min. In Fig. 6 the preview of the engineered microwave reactor is presented. Test will be conducted for determining the best volume of liquid to use for each run of treatment. If a volume to be digested smaller than 60 lt/run will be chosen, the magnetron on the top of the reactor will be moved to the side entry in order to have a better microwave irradiation. A set of three blades will be used for continuous stirring of the mixture. The oxidant/mixture ratio will be the most important parameter that will change in relation to the "strength" of the leachate to be treated. A catalyzed Fenton's-like reaction will be tested for the strongest ones.

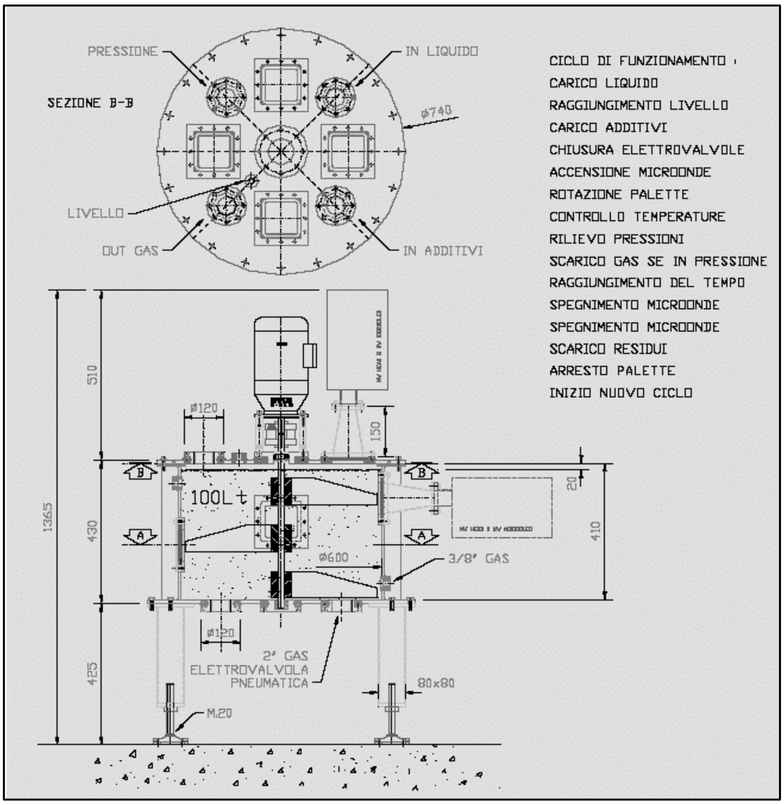


*Fig.6. Pilot-scale microwave assisted reactor engineered for the on site leachate organic digestion step.*

An ultra/nano filtration or a reverse osmosis unit could also be integrated on site as final treatment for the pre-treated liquid to be securely disposed without the need of further off-site treatments.

## CONCLUSIONS

In January 2004 the weekly sampling of leachate from the selected cells and lots has been started. An analytical method has been developed for laboratory samples pre-treatment. Preparation of the filters for analysis with optical and electron microscopes (University of Venice and ISPESL) are currently in progress. Analyses will be carried out progressively during samplings and in parallel between the two partners for appropriate comparison.

If the presence of large amounts of asbestos fibers in landfill leachate will be confirmed, the possibility of experimenting a real dedicated on-site process for asbestos-containing leachate treatment will be considered. This allows closing the asbestos-cycle at the landfill site avoiding transfer to the wastewater facility with related risks.
The onsite process could be used for dedicated leachate treatment when dedicated cells are involved and an efficient disposal plan for the landfill management is foreseen.

**BIBLIOGRAPHY**

(1) F. Paglietti, L. Zamengo, S. Polizzi, M. Giangrasso, G. Fasciani. CNR Conference Proceedings "L'industria e l'amianto" Roma, 26-28 November 2002.

(2) Decreto Legislativo del Governo n° 277 del 15/08/1991. Attuazione delle direttive n. 80/1107/CEE, n. 82/605/CEE, n. 83/477/CEE, n. 86/188/CEE e n. 88/642/CEE, in materia di protezione dei lavoratori contro i rischi derivanti da esposizione ad agenti chimici, fisici e biologici durante il lavoro.

(3) EPA 100.1 Chatfield, Dillon. Analytical method for determination of asbestos fibers in water. EPA 600483043, 1983.

(4) G. Brandi, M. Sisti, G. Amagliani. Evaluation of the enviromental impact of microbial aerosols generated by wastewater treatment plants utilizing different aeration systems. Journal of Applied Microbiology 2000, **88**; 845-852