

CHEMICAL AND ECOTOXICOLOGICAL LONG-TERM BEHAVIOUR OF NEW MATERIALS FOR QUARRY BACK-FILLING AND UNDERGROUND CONSTRUCTIONS

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Abstract ID Number: 186

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Abstract

The main aim of the Valomat project was the development of new materials for quarry back-filling and underground constructions, based on the reuse of bottom ashes from MSWI. Bottom ashes were collected in six incineration plants of Europe. Some of them were selected for the development of new materials.

One task of this project comprised the study of the long-term behavior of new materials, under simulated conditions of environmental exposure. Three different scenarios were studied. For each scenario, a pilot plant was constructed and the new materials were studied under laboratory conditions or natural weather. The long-term behavior of these materials was assessed through the characterization of chemical and ecotoxicological properties of the leachates.

The chemical contamination and the ecotoxicological levels of the leachates were relatively low, although different levels had been determined for the three different scenarios. The immersion in dechlorinated tap water (scenario S1) had shown the highest emission levels of chlorides, sulphates, DOC, and Al, especially for the materials B2/1 and B2/2. The lowest ecotoxicological and chemical levels were determined in the scenario in which the materials were buried in a sieved soil.

Key words: MSWI bottom ashes; New materials; Quarry back-filling; Underground constructions; Chemical and ecotoxicological long-term behaviour

1. INTRODUCTION

The increasing adoption of incineration technology for the treatment and energetic valorisation of Municipal Solid Wastes (MSW), especially in Europe, has promoted the increment of the amounts of ashes produced [1, 2, 3].

The valorisation of bottom ashes has become a strong technical possibility for the reduction of the amounts of ashes to be land-filled. A new field for bottom ash valorisation has been developed in France by Inertec and Soletanche-Bachy companies: new materials for mine and quarry back-filling. This new valorisation field, jointly with the concrete production for underground low strength applications, were the two main subjects of study in Valomat project.

This project was approved by the EC, in 1998, in the framework of Brite-Euram III project. The project was developed in six main steps. One of these steps was the long term assessment of the chemical and ecotoxicological behaviour of the new materials. This paper will be focused in the results obtained in this study.

The methodology developed was based on the European Standard ENV 12920 [4]. This standard defines a methodology for the assessment of the leaching behaviour of residues, or materials containing residues, under specific conditions.

2. MATERIAL AND METHODS

2.1. Tested materials and scenarios of application

The materials shown in Table 1 were studied for long term behaviour.

Table 1: General composition of the new materials and application fields

Material code	BA code	BA/FA/HB and other reagents (% wm)	Water (%)	Application
B2/1	B2	70/14/5	11	MQB
B2/2	B2	73/11/5	11	MQB
B3/1	B3	46/30/20	4	DW

BA: bottom ash; wm: wet matter; FA: fine aggregates; HB: hydraulic binders; MQB: mine and quarry back-filling; DW: diaphragm walls

The fine aggregates were the following: a) B2/1 – fly ashes not produced in MSW incineration plants; b) B2/2 – slag from ore treatment; c) B3/1 – fine sand.

2.2. Environmental exposure of new materials

It was assumed that the scenario in which the highest environmental exposure would take place comprised a quarry with the bottom below the aquifer surface. The quarry back-filling would be done by pumping the new materials from the bottom ash stabilisation plant to the bottom of the quarry. The filling process should be carried out in overlaid layers which would be in contact with the atmosphere. The carbon dioxide in the atmosphere is, in this case, important for the carbonation of these materials and the leaching process is carried out by direct raining. This scenario was designated as S3.

After the pit fulfilling, a soil layer would be placed over the materials. The aquifer would achieve its normal depth. In this situation, two scenarios were considered: 1) Scenario S2 – in which the new materials were in direct contact with natural soil. The leaching process would be carried out by the percolating water through the soil. 2) Scenario S1 – in which a direct contact of the aquifer with the new materials would take place. For the diaphragm wall application was considered one scenario. This was the worst scenario of environmental exposure (Scenario S1).

2.3. Pilots constructed for the simulation of scenarios S1, S2 and S3

To simulate the scenarios described above, three sets of pilots were constructed (Figure 1).

2.4. Soil used in pilots P5 to P7

The soil used in pilots P5 to P7 was collected at the *campus* of FCT/UNL, near an experimental site for the cultivation of Sweet Sorghum. It was sieved through a mesh of 4 mm. This soil had alkaline properties (pH in water = 8.8; pH in KCl = 8.4; carbonates = 24% dry matter). The contents of N-Kjeldahl, total phosphorus and organic carbon were low (N-Kjeldahl

= 0.89 g.kg⁻¹ dry matter (dm); total phosphorus = 0.55 g.kg⁻¹ dm; organic carbon = 0.2 % dm). The moisture content was 19% (w/w) and the conductivity in water was of 0.109 mS.cm⁻¹.

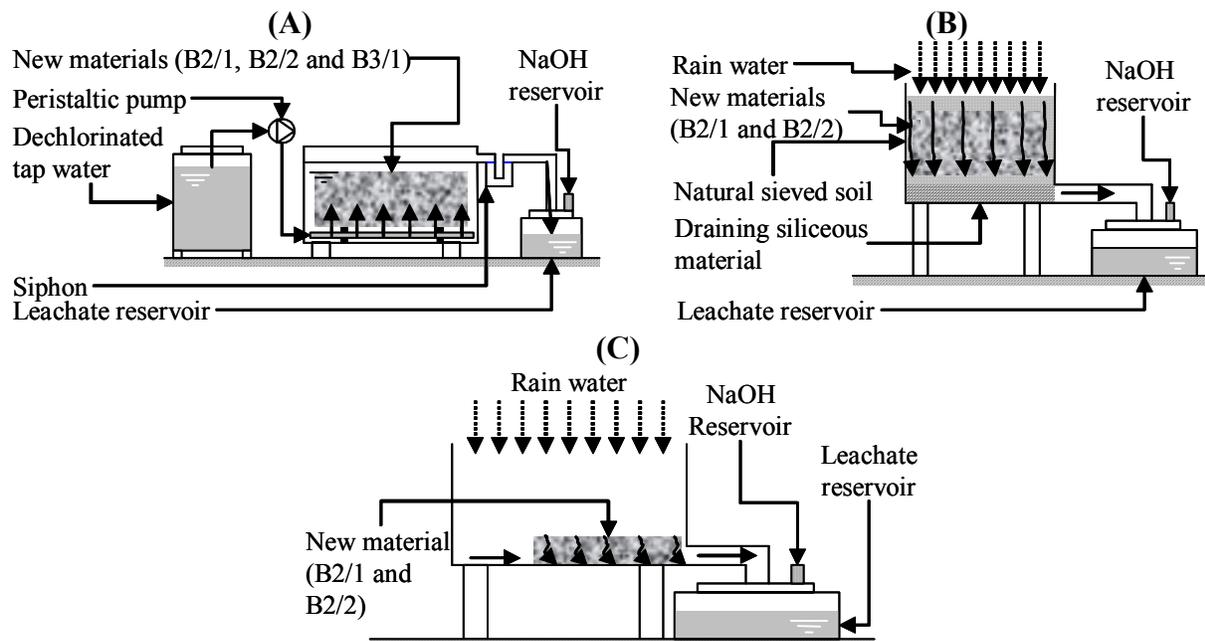


Figure 1: Diagram of pilots P1 to P10 constructed for the simulation of scenario S1 (A), S2 (B) and S3 (C) (blank tests were carried out in pilots P4 and P7, with PVC boxes as sample, and P10, without any material as sample)

These parameters were analysed according to the following standards: carbonates – NF ISO 10693; conductivity - NF ISO 11265; organic carbon - Walkley and Black method; moisture content - NF ISO 11465; N-Kjeldahl - APHA *et al.* [5] (volumetric method using boric acid and sulphuric acid); pH (1:10 in water and 1:5 KCl) - NF ISO 10390; total phosphorus - APHA *et al.* [5] (colorimetric method after digestion with sulphuric acid).

2.5. Chemical characterisation of leachates

The water flowing into the pilots (dechlorinated tap water and natural rain water) and the leachates flowing out the pilots were characterised for the following parameters: chlorides (ISO 9297); dissolved organic carbon (DOC) (ISO 8245); conductivity (ISO 7888); N-NH₄⁺ (APHA *et al.* [5] – volumetric method by using ascorbic acid and sulphuric acid); pH (APHA *et al.* [5] – potentiometric method); SO₄²⁻ (APHA *et al.* [5] – turbidimetric method); Al (APHA *et al.* [5] – AAS with flame after reaction with 8-hydroxyquinoline and extraction with MIBK); As (APHA *et al.* [5] – hydride generation and quantification by AAS); Cd, Cu, Ni, Pb and Zn (ISO 8288); Cr total (ISO 9174: method A); Cr VI (NF T 90-043); Fe (APHA *et al.* [5] – AAS with flame); Hg (ISO 5666/1).

2.6. Ecotoxicological characterisation of leachates

The following ecotoxicological assays were used: a) luminiscence inhibition of *Vibrio fischeri* (ISO 11348-3); b) mobility inhibition of *Daphnia magna* (ISO 6341); c) growth inhibition of *Pseudokirchneriella subcapitata* (ISO 8692); d) germination inhibition of *Lactuca sativa* (NF X31-201).

The EC₅₀ values for *P. phosphoreum* were determined through the mathematical relationship between the concentration of a toxic substance and the response of this organism in terms of light emission. The growth inhibition of the alga *P. subcapitata* was assessed through the specific growth rate in culture media with different initial concentrations of the eluates. A direct correlation curve was previously established between the number of cells and the absorbance (560 nm). The EC₅₀ values for *P. subcapitata* were determined through a linear regression over a semi-logarithm plot, using the methodology of the least squares. The EC₅₀ values for *D. magna* and the IC₅₀ values for *L. sativa* were determined through the *probit* method (USEPA Probit Analysis Program, version 1.5). The Aquaculture Department of the Portuguese Institute for Maritime Research (IPIMAR) has supplied the species *P. subcapitata* and *D. magna*. Microbics Corporation has supplied the bacterium *P. phosphoreum* and Germiplanta Company the lettuce seeds.

3. RESULTS AND DISCUSSION

3.1. Scenario S1

3.1.1 Chemical characterisation of leachates

Figure 2 shows the evolution of the pH values and the concentration of chlorides, sulphates and Al in the influent water and in the leachates of the pilots P1 to P4.

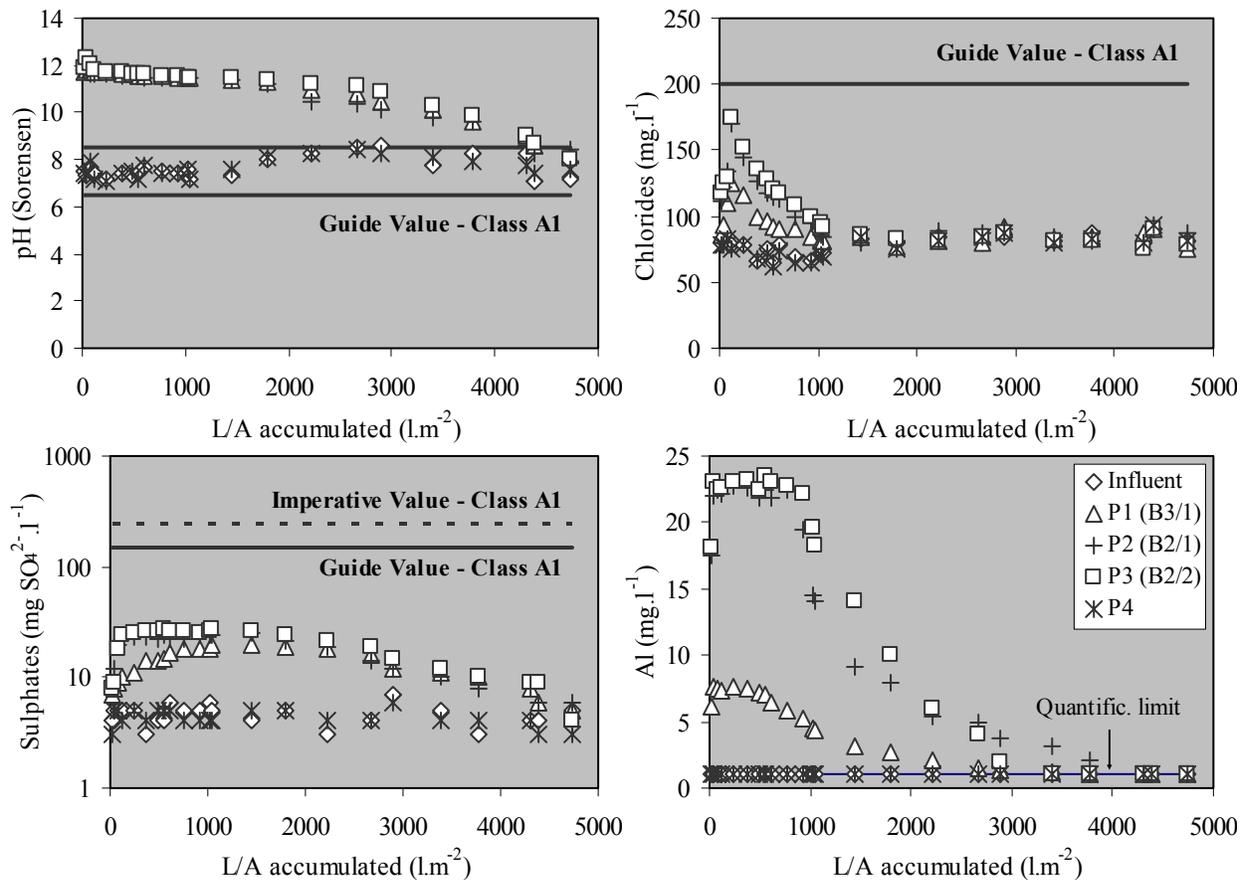


Figure 2: pH values and concentrations of chloride, sulphate and Al in the influent water and leachates of pilots P1 to P4

In Figure 2 it was also drawn, when available, the guide and imperative values for surface water systems used for the production of water for human consumption. Among the three classes of water quality defined in the Council Directive number 75/440/CEE, it was selected the class associated with the highest quality (class A1).

The leachates of the materials studied have shown alkaline properties. The initial pH values were approximately around 12. A progressive decrease of pH was observed with the increase of L/A ratio. This decrease was more significant for L/A ratios above 2000 l.m⁻². The pH values of the leachates were closer to the pH value of the influent water at the end of the assay (accumulated L/A = 4700 l.m⁻²; time of assay = 380 days). All over the assay, the leachates of the pilots P1 to P3 were characterised by pH values higher than the upper Guide Value defined for pH (8.5). It is important to refer that these pH values are common to materials based on cement matrices [1].

The immersion of the stabilised/solidified (S/S) materials in the leachant agent has conducted to a rapid release of the chemical species weakly bound to the solid matrices. This release is mainly controlled by the dissolution constants of highly soluble chemical species. The release based on the dissolution was observed for chlorides, DOC (not shown) and, for a certain extent, for sulphates. This release was characterised by a significant increase in the concentrations of this chemical species in the leachates of the pilots. The increase in those concentrations was observed for the first accumulated L/A ratios, generally comprised between 20 and 119 l.m⁻². The increase of the release of salts was followed by a decrease of their concentration in the leachates. This can be explained by the decrease of the available salts in the layers directly in contact with the leachant. In this phase, the emission was controlled by diffusion processes from the S/S matrices.

Among the metals analysed, only Al was detected above the quantification limit. The release of this metal seemed to be diffusively controlled. An important decrease of Al concentration in the leachates was observed after a L/A ratio of 800 l.m⁻², probably due to the decrease of available Al in the layers directly in contact with the leachant. In a general way, the release of salts and Al was higher in the materials B2/1 and B2/2, probably due to the higher content of bottom ashes and the lower content of hydraulic binders present in these materials.

3.1.2 Ecotoxicological characterisation of leachates

Figure 3 shows the ecotoxicological levels determined in the leachates of the pilots P1 to P3.

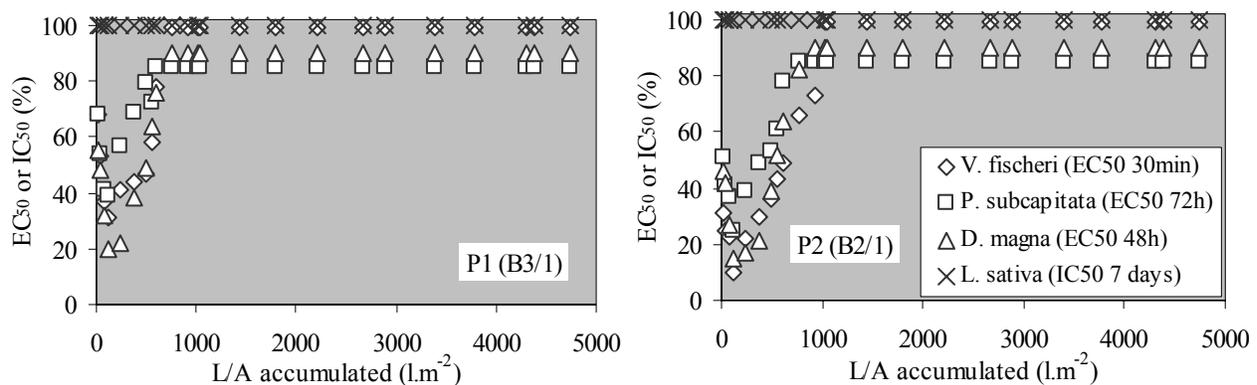


Figure 3: Ecotoxicological characterisation of the leachates of pilots P1 to P3

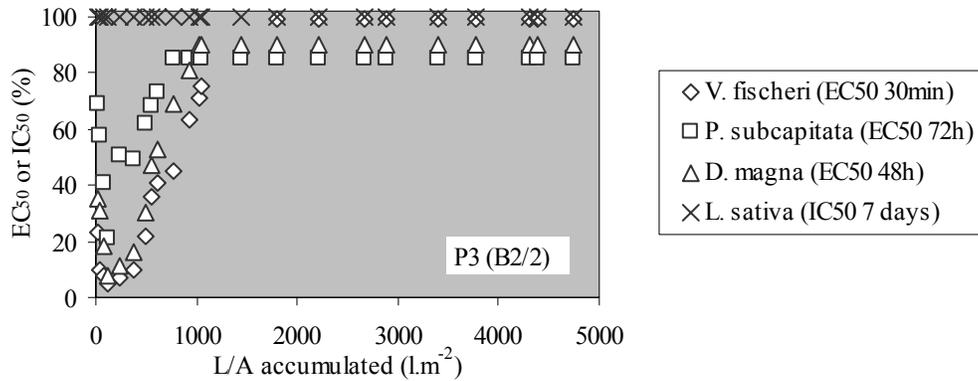


Figure 3: (continued)

The germination of *L. sativa* was not affected by the ecotoxicological levels of the leachates. For the other biological indicators, an increase in the ecotoxicological levels of the leachates was observed till the L/A ratio of 119 l.m⁻². After the lowest ecotoxicological levels have been observed, it was registered an increase of the EC₅₀. In a general way, no significant levels of ecotoxicity were determined after a L/A ratio of 1000 l.m⁻². This variation in the EC₅₀ seemed to be related with the variation in the emission levels of salts and Al observed in the chemical characterisation of leachates.

3.2. Scenario S2

3.2.1 Chemical characterisation of leachates

Figure 4 shows the variation of pH, chlorides, sulphates and DOC in the rain water (P10) and in the leachates of pilots P5 to P7. It is important to stress that the emission of chlorides, sulphates and COD were similar to the emission pattern observed for pilots P2 and P3. This was characterised for the occurrence of concentrations peaks for low L/A ratios comprised in the interval of 40 to 50 l.m⁻².

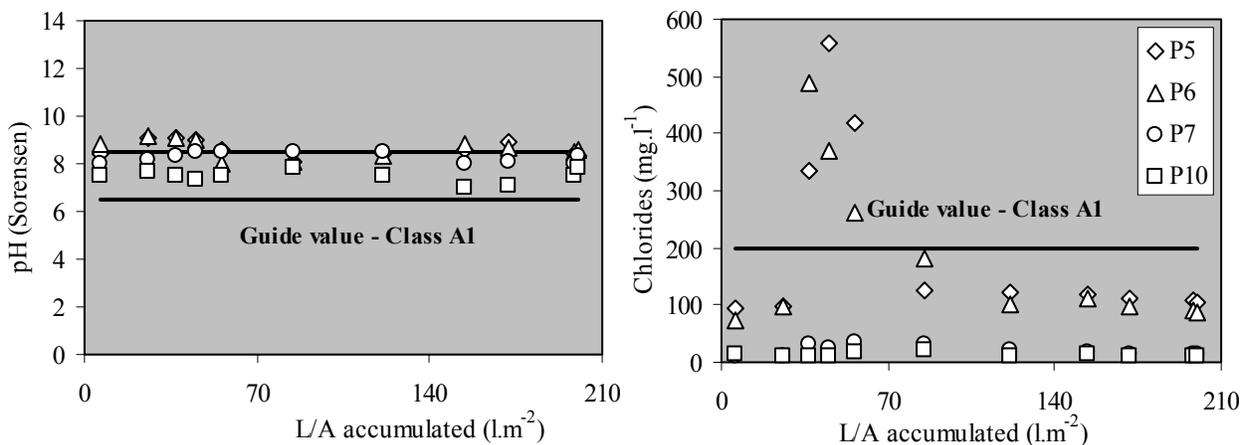


Figure 4: pH values and concentrations of chlorides, sulphates and DOC in rain water (P10) and in the leachates of pilots P5 to P7

After these peaks have been achieved, decreasing phases were observed for all these four chemical parameters.

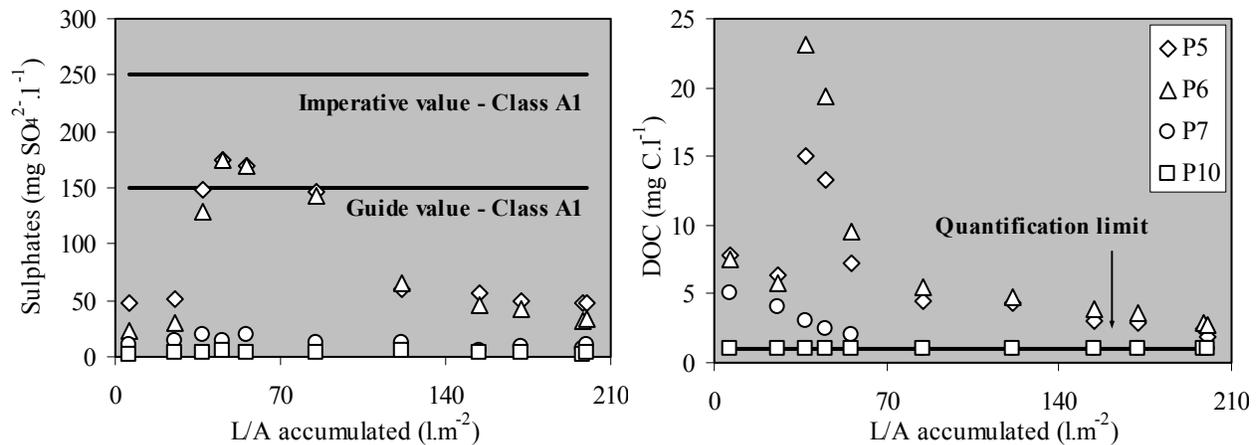


Figure 4: (continued)

Following these phases, the emission levels were characterised by low and constant emission rates. In a similar way of what it was referred for pilots P2 and P3, this emission pattern of chlorides, COD and sulphates is characteristic of the chemical species with high solubility in water. Once the leaching agent applied to the pilots P5 and P6 (rain water) was sub-saturated in chloride, sulphate and COD (pilot P10), the solubility of this chemical species occurred at high rates.

It is important to refer that the soil used in pilots P5 to P7 had shown a high capability of reducing the pH values of the leachates, which were characteristic of the materials B2/1 and B2/2. The contact of the new materials with the soil allowed the production of leachates with pH values lower than 9.0. The pH of the soil in water (8.8) was in the range in which several metallic elements, whose solubility is pH-dependent, show a reduced solubility. The Al makes part of this group, being possible to assume that the pH of the leachant, induced by the moderated alkaline properties of the soil, had not contributed to the increment of the solubility of this metal.

3.2.2 Ecotoxicological characterisation of leachates

In Figure 5 it is shown the ecotoxicological levels of the leachates of pilots P5 and P6. The ecotoxicological levels determined in the leachates of pilots P7 and P10 are not shown because they were above the sensitivity limits of all bio-indicators used.

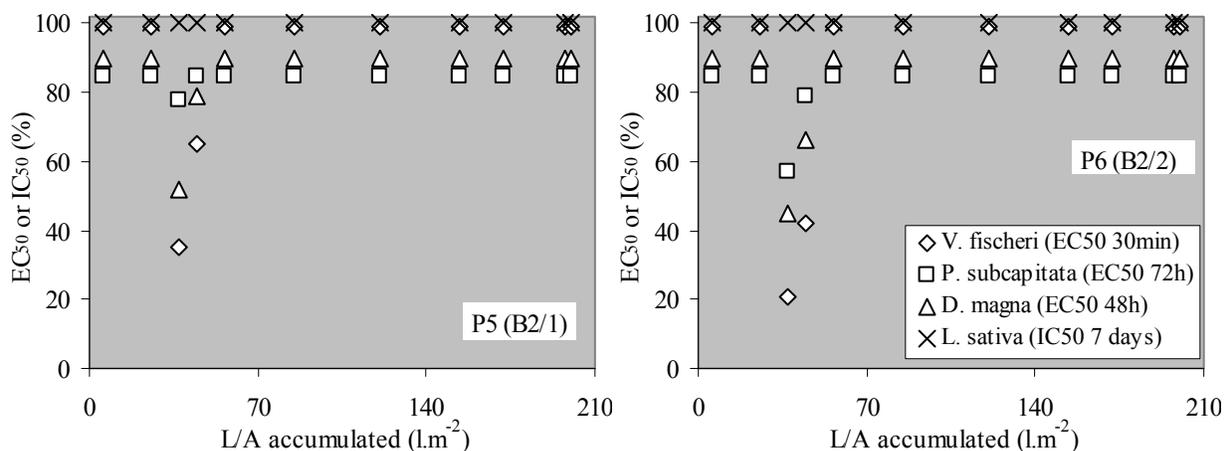


Figure 5: Ecotoxicological characterisation of the leachates of pilots P5 and P6

The ecotoxicological results determined in the leachates of pilots P5 and P6 were quite reduced or even undetectable. For both materials B2/1 and B2/2, only for the L/A ratios of 37 and 45 l.m⁻² it was observed levels of ecotoxicity below the sensitivity limit of the biological indicators. Nevertheless, these ecotoxicological levels were low and can be classified under the class 2 of the Toxicity Classification System (TCS) developed by Professor Persoone. The ecotoxicological levels belonging to this class are classified as not significant levels of ecotoxicity. The L/A ratios, in which ecotoxicological effects were detected, were coincident with the highest concentration of chlorides, sulphates and DOC.

For the bio-indicators *V. fischeri*, *P. subcapitata* and *D. magna*, the ecotoxicological levels determined in the leachates of the material B2/1 (pilot P5) were lower than for the leachates of the material B2/2 (pilot P6). These results fit with those obtained for the same materials when exposed to the scenario S1. It is important to stress that for both materials the ecotoxicity measured in the peaks of emission were much lower in scenario S2 than in scenario S1.

3.3. Scenario S3

3.3.1 Chemical characterisation of leachates

Figure 6 shows the variation of pH, chlorides, DOC and Al in the leachates of pilots P8 and P9.

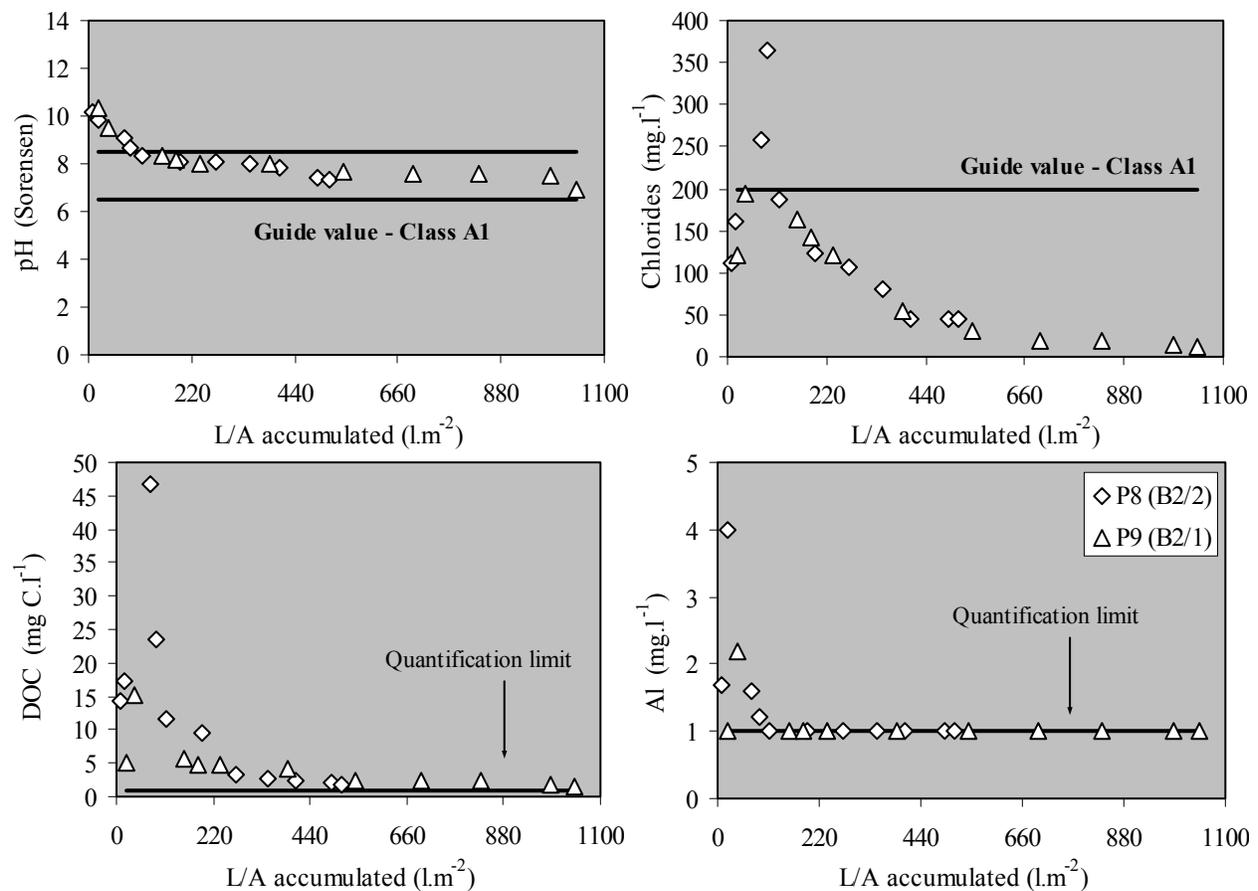


Figure 6: pH values and concentrations of chlorides, DOC and Al in the leachates of pilots P8 and P9

The evolution of the conductivity (not shown), chlorides, DOC, sulphates (not shown) and Al were characterised by different phases. The initial phase was characterised by an increase of the values or concentrations of parameters. This phase had occurred from the beginning of the assay till the L/A ratio of 100 l.m⁻². For Al, the concentration peaks were observed earlier than for the other chemical species (L/A=19.6 and 41.2 l.m⁻² for materials B2/2 and B2/1, respectively). The second phase was characterised by a rapid decrease of their values or concentrations till a L/A ratio of 200 l.m⁻². For Al, this second phase was shorter, possibly due to the rapid decrease of pH values. From this phase on, the release of chlorides, DOC and sulphates had occurred at lower emission rates. This final phase had occurred till the end of the assay.

The pH evolution in both pilots had shown a rapid decrease in its values for the first L/A ratios. The decrease has occurred from values close to 10.5 to values of about 8.5, for L/A ratios from 10 to 88 l.m⁻², in pilot P8, and from 21 to 156 l.m⁻², in pilot P9. In these ranges of L/A ratios, the pH values had possibly promoted the mobilisation of Al. No other metal than Al was detected in the leachates of pilots P8 and P9 above the quantification limits.

3.3.2 Ecotoxicological characterisation of leachates

Figure 7 shows the results obtained in the ecotoxicological characterisation of the leachates of pilots P8 and P9.

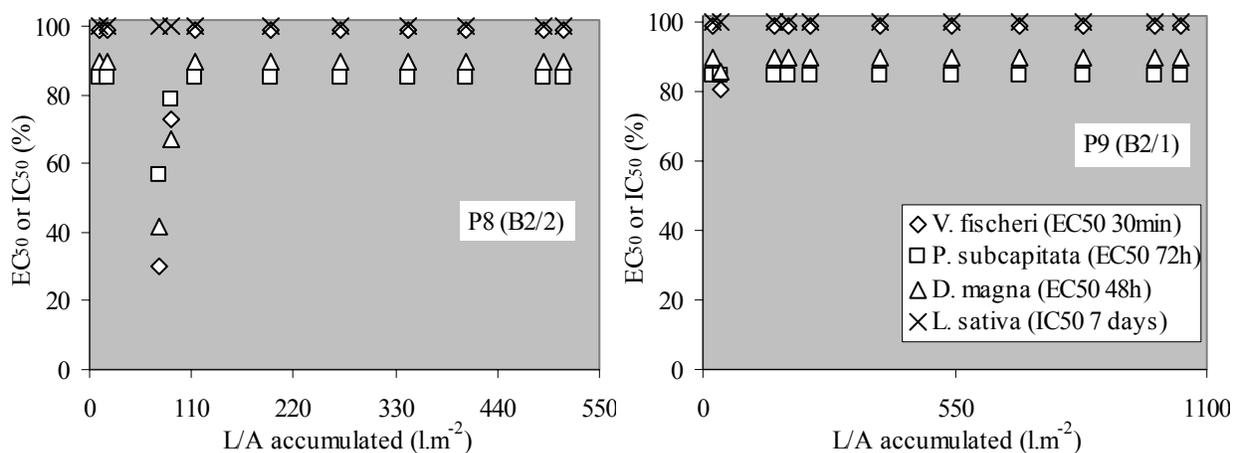


Figure 7: Ecotoxicological characterisation of the leachates of pilots P8 and P9

It was possible to detect ecotoxicity in the leachates of both pilots for the others bio-indicators. The ecotoxicological levels detected were low, being classified under the class 2 of TCS (no significant levels of ecotoxicity). Comparing the ecotoxicological levels obtained in the leachates of scenario S3 with the levels determined for the other scenarios, it is possible to conclude that the levels obtained in scenario S3 were similar to those observed in the leachates of scenario S2, in terms of their intensity and in terms of their evolution as function of the accumulated L/A ratios.

The highest ecotoxicological levels were determined in the leachates of the materials B2/1 and B2/2, when immersed in dechlorinated water (scenario S1). For scenario S1, the intensity of the ecotoxicological levels was higher and the detection of the levels effectively quantifiable was more extended along the accumulated L/A ratios. Hence, it is possible to conclude that the materials B2/1 and B2/2 has shown more stable ecotoxicological behaviour in the scenarios S2 and S3.

4. CONCLUSIONS

The chemical contamination and the ecotoxicological levels of the leachates were low, although different levels had been determined for the three different scenarios of exposure.

For each scenario, different levels had been observed among the new materials analysed. The immersion in dechlorinated water (scenario S1) had shown the highest emission levels of chlorides, sulphates, DOC and Al, especially for the materials B2/1 and B2/2. The ecotoxicological levels of the leachates of materials B2/1 and B2/2, produced under the scenario S1, were the highest ones determined for all scenarios. The range of L/A ratios in which it was observed ecotoxicity was much longer for this scenario than for any other one. The material B3/1 had shown, under the water immersion scenario a more reduced emission of chemical substances and lower ecotoxicological levels than the materials B2/1 and B2/2. This is probably related with the higher chemical stability of this material, due to the higher content in hydraulic binders and to the lower amounts of bottom ashes.

The lower emission rates from the materials B2/1 and B2/2 and the lower ecotoxicological levels of the leachates were observed for the exposure scenario S2.

It is important to stress that the chemical contamination and the ecotoxicological levels of the leachates, determined in the pilots used in this assay, may not be representative of the levels effectively measured at target ecosystems, located downstream the place of the application of the materials. These levels are representative of those that may be registered in the surrounding environments of the materials. The dilution factors in soils and aquatic environments, the sorption/desorption processes and the biological reactions in natural environments may play an important role in the change of these chemical and ecotoxicological levels. These chemical and biological effects must be taken into account in an ecological risk assessment of these materials.

ACKNOWLEDGMENTS

The authors would like to acknowledge the European Commission for having supported the Valomat project (BE-97-5128) through the Brite-Euram III program under which this work was done.

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