

THE TREATMENT OF LEAD-CONTAMINATED TRAVERTINE

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ABSTRACT

In the urban sites the lead addition in petrol, as an antidetonation agent, allows pollution of exposed surfaces of buildings, soils and vegetation. In a preliminary way a research work has been carried out simulating lead pollution of the slab surfaces of the Roman-Travertine stone. The Roman-Travertine is a limestone dimensional stone widely employed in Italy especially for dressing of the old buildings in Rome.

Results achieved by laboratory leaching tests have put in evidence the potential for lead removing from slab surfaces by means of ammonium acetate solutions. Higher lead removal has been obtained for higher temperatures and concentrations of leaching solutions. More than 90% of the lead adsorption has been extracted from polluted stones coming from dismantling of buildings; on the contrary, the limestone rock was poorly affected by that leaching agent.

LEAD CONTAMINATION OF SOIL

Lead pollution of the environment derives mainly from exhausts of cars using petrol containing tetramethyle and tetraethyle lead as knock suppressers, from industrial effluents using lead or lead compounds and from primary and secondary metallurgical waste. In some areas water pollution (especially water rich in oxygen, in carbonic acid and in nitrates that facilitate lead solubility) is due to the use of old mains made of lead or of lead alloys.

Environmental pollution has repercussions on man, who can absorb lead from the air, from water and from foodstuffs. In fact, whatever its source, lead pollutes the air, deposits in the soil and in vegetation and thus reaches man directly and indirectly. Lead concentration in foodstuffs can increase due to the containers in which food is preserved (lead-soldered boxes) and occasionally to protracted use of crockery coated with lead enamel and paints (Abbritti, 1988). Table 1 gives the average contents of the most common metals found in soil and plants (Sequi, 1989; Kabata Pendias et al., 1985; Canova et al., 1995).

The lead concentration rates found in street dust largely exceed the average soil rates, ranging between 1600 and 2500 mg/kg (Cariola et al., 1992). Analyses carried out on soil

taken from firing ranges and from metallurgical sites evince the presence of lead cations, above all in the smaller (< 20 µm) and in the larger (> 6000 µm) size classes, while lead concentrations decrease in median particle size classes (Pruijn et al., 1993). In fact, in soil taken from a firing range the surface soil layer was polluted with balls of lead shot, that also undergo a process of leaching by atmospheric agents. In this way the leached lead is re-absorbed by the clay fraction and the organic matter in the soil. The shots undergo further reduction in size due to mechanical actions and corrosion. Conversely, in soil polluted by residue of industrial metallurgical activity the waste is easily visible, is lighter in weight than the mineral constituents of the soil and in part reduced in size due to the action of atmospheric agents.

GENERAL FEATURES OF THE LEAD EXTRACTION PROCESSES

Most of the soil decontamination processes can be classified in one of the following groups (Bunge et al., 1995):

- biological treatments;
- thermal treatments;
- immobilization;
- soil washing.

Metal	Average concentration in soil (mg/kg)	Average concentration in plants (mg/kg)
Cadmium	0.01 : 20	0.07 : 0.28
Chromium (III)	5 : 1500	0.02 : 0.2
Manganese	20 : 10000	30 : 500
Mercury	0.01 : 0.5	0.0006 : 0.086
Nickel	10 : 100	0.2 : 3.7
Lead	16 : 80	0.05 : 3.0
Copper	2 : 250	1 : 20
Zinc	1 : 900	1 : 73

Table 1. Average contents of heavy metals in soil and plants.

In the case of soil pollution by heavy metals, thermal treatments do not give good results (except for mercury) while they give satisfactory results in all cases of pollution by organic substances in all kinds of soil (Bunge et al., 1995).

The remediation processes can further be classified in two general categories: treatments *in situ* and treatments *ex situ* (EPA, 1996):

- the former type is carried out on the site without removing the soil;
- the latter type entail removal of the contaminated soil.

The separation by size of the contaminated soil particles is useful in *ex situ* treatments inasmuch as it enables reduction of the volume of contaminated soil, often comprised above all of the smallest particles (Prujin et al., 1993; Bunge et al., 1995). In both *in situ* soil treatment processes and *ex situ* soil washing, chemical reagents are used to improve extraction of the contaminants (Benker, 1995). In the processes, in which chemical compounds act in the removal of the heavy metals in the soil, are involved (Palmer et al., 1996):

- competition in the sites of adsorption by chemical agents acting on the surfaces of solids;
- complexation with chemical agents.

Studies undertaken in a laboratory scale of soil washing using chemical agents on samples of lead polluted soil have demonstrated the efficacy of 1 N solutions of HCl and 0.01 M solutions of EDTA: it gave lead removal of 92.5 % and 93.5 % respectively, while solutions of 1 N of CH_3COOH and solutions of 1 M of CaCl_2 gave removal of 57.3 % and 47.2 % respectively (Cline et al., 1995). Lead decontamination in sites in which car batteries are stocked, has been realised both by soil washing techniques (EPA, 1996) and by *in situ* leaching techniques utilising chemical agents (Skinner et al., 1992).

REMOION OF LEAD POLLUTION FROM TRAVERTINE SLABS

Travertine is an ornamental dimensional stone, essentially calcium carbonate, widely used, especially in Rome, due to its being easily cut in slabs or hewn, easily polished if used indoors and highly durable when used for outdoor fittings of

buildings. The impact of urban car traffic on travertine is degradation and in particular lead contamination by the knock suppresser agents contained in petrol.

In order to verify the possibility of removing lead from the surface of travertine used as fitting for building exteriors contaminated by car exhausts, different series of leaching experiments were carried out on laboratory scale. Travertine slabs, coming from the Tivoli area in the Lazio region, were reduced in size in order to increase their specific surface and to enhance the laboratory results. The flakes were placed in glass columns and subjected to a flow of the leaching solutions for fixed periods of time during which the amounts of lead extracted were recorded. The leaching tests were carried out using 7 cm glass cylinder columns. The columns were filled at the bottom with 4 cm diameter glass balls, kept down with a perforated baffle plate to stop the flow carrying away the finer flakes. To reduce the possible formation of fixed paths of the leaching solution in the travertine bed a waterhead adjustable in height by drainage flow regulation was kept. Figure 1 shows the experiment apparatus utilised, while figure 2 is a schematic description of the elements composing the leaching circuit.

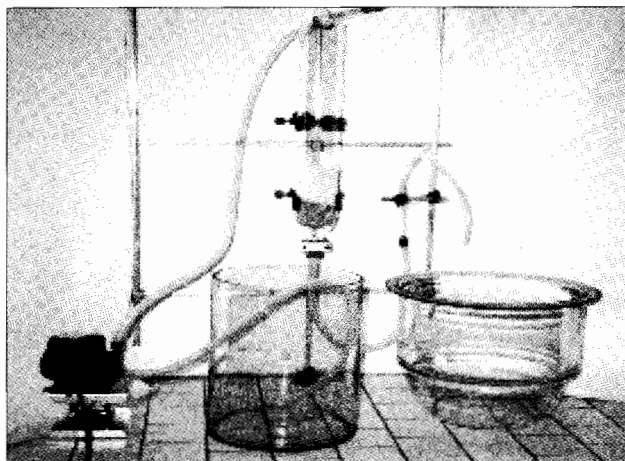


Figure 1. Experimental apparatus for the leaching tests.

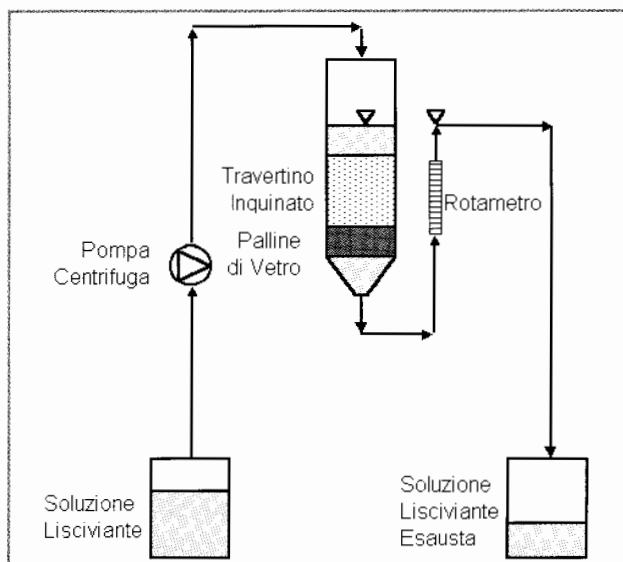


Figure 2. Schematic description of the leaching circuit.

An open circuit was operated in order to simulate in situ soil decontamination processes. In all the experiments the leaching solutions were recovered after one flow through the contaminated material. Once recovered the solutions have to be regenerated by extracting the leached lead and then reused in further treatments.

EXPERIMENTAL PROCEDURES

In order to increase the specific surface and to enhance laboratory results, slabs of travertine were reduced to less than 2 mm. The size distribution obtained is recorded in figure 3.

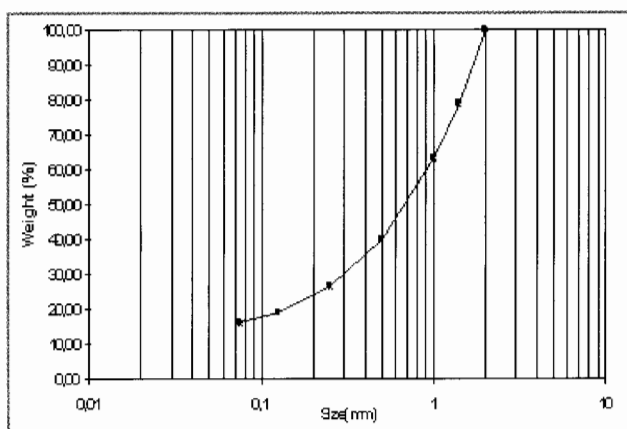


Figure 3. Size distribution of the crushed travertine slabs.

Particles below 0.25 mm in size were eliminated before column leaching in order to avoid bundling of the material and dragging of the finer particles in the leaching solution.

In order to simulate the conditions of lead contamination on travertine, $PbCl_2$ was added: in fact the lead is found in car exhausts as chloride compounds.

To the flakes of travertine a solution of $PbCl_2$ at 500 ppm lead concentration was added: a rate of 1 g Pb per kg travertine was adopted in the first series of experiments and 100 mg Pb per kg travertine in the second series of experiments. The travertine thus polluted was then dried at 75 °C for minimum 3 days. The state of contamination was further checked by means of spectrometric analysis of samples of polluted flakes of travertine (ICPAES-ICP 400 Perkin Elmer).

The leaching agents were selected taking into account the difficulties encountered in decontamination of limestone soils (EPA-Report, 1994).

In fact, cations of heavy metals that contaminate soils are more easily removed using acid solutions. On the other hand, using pH acid solutions causes dissolution of the carbonate constituents of travertine.

Thus it was chosen to operate using the following agents:

- distilled water;
- distilled water with added CO_2 ;

- oxalic acid solution (at 0.1 % weight);
- solutions of ammonium acetate at different concentrations;
- (solid to be leached)/(leaching solution) weight ratio = 1:20 (i.e. 400 g of solid and 8 liters of leaching solution).

The leaching solution was fed to the bed of solid for leaching with a constant flow rate of 100, 50 and 25 cm^3/min using an open circuit.

During the experiments samples of the solution following percolation were taken at regular time intervals in order to measure the lead extracted and the calcium dissolved; the fluids were also tested for pH.

Table 2 itemises the experimental conditions adopted in the different cases.

Table 3 records the percentages of lead extraction in the experiments performed under the different conditions, starting from the travertine contaminated by 1000 ppm Pb. An experiment was carried out starting from travertine contaminated by 100 ppm Pb.

Material	Pb (ppm)	Leaching agent	Leaching Conditions	
			Temperature (°C)	Flow rate (cm^3/min)
Travertine	1000	Water	22	100
Travertine	1000	Water + CO_2	22	100
Travertine	1000	Oxalic acid 1%	22	100
Travertine	1000	Ammonium acetate 1%	22	100
Travertine	1000	Ammonium acetate 5%	22	100
Travertine	1000	Ammonium acetate 10%	22	100
Travertine	1000	Ammonium acetate 20%	22	100
Travertine	1000	Ammonium acetate 10%	22	50
Travertine	1000	Ammonium acetate 10%	22	25
Travertine	1000	Ammonium acetate 10%	35	100
Travertine	1000	Ammonium acetate 10%	50	100
Travertine	100	Ammonium acetate 20%	22	100

Table 2. Experimental procedures adopted for the removal of lead from travertine.

Figures 4, 5 and 6 give the patterns of lead extraction over time in the leaching experiments with travertine contaminated by 1000 ppm Pb.

The leaching experiments demonstrated the efficacy of ammonium acetate solutions for extracting lead from travertine.

Furthermore, lead extraction is enhanced by increasing:

- the concentration of ammonium acetate in the leaching solution;
- the temperature of the leaching solution;
- the flow rate of the leaching solution.

Experimental conditions	Leaching agent										
	W	CO ₂	OA	Ammonium acetate							
Leaching concentration (%)			0.1	1	5	10	10	10	10	10	10
Temperature (°C)	22	22	22	22	22	22	22	22	22	35	50
Flow rate (cm ³ /min)	100	100	10	100	100	100	100	25	50	100	100
Lead extracted (%)	0.14	0.34	0.67	0.45	39.7	81.15	95.84	41.64	58.02	86.94	96.92

Table 3. Percentages of lead extracted from travertine contaminated by 1000 ppm of lead cation (W = distilled water, CO₂ = water saturated with CO₂; OA = oxalic acid).

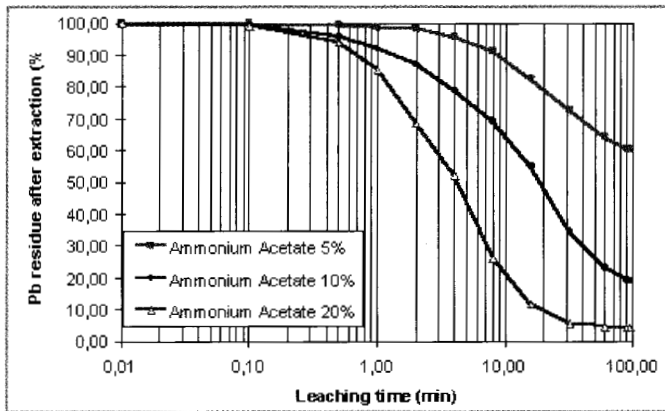


Figure 4. Patterns of lead extraction over time in terms of concentration variations of ammonium acetate in the leaching solution (T = 22°C; Q = 100 cm³/min). Travertine polluted by 1000 ppm Pb.

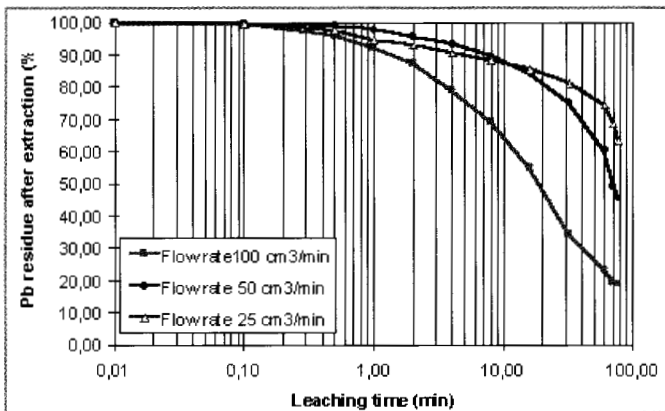


Figure 5. Patterns of lead extraction over time in terms of variations of leaching solution flow rate (T = 22°C; ammonium acetate = 10%). Travertine polluted by 1000 ppm Pb.

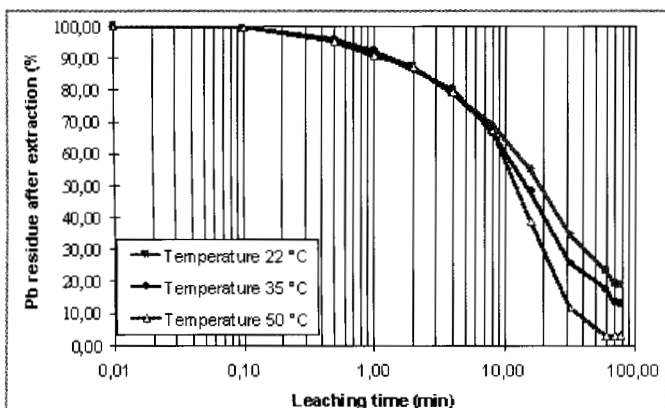


Figure 6. Patterns of lead extraction over time in terms of temperature variations of leaching solution (Q = 100 cm³/min; ammonium acetate = 10%). Travertine polluted by 1000 ppm Pb.

In order to verify the results also in the case of very low concentrations of polluting lead a series of experiments was conducted on a sample of travertine polluted by 100 ppm of lead. The conditions for this experiment were:

- 20 % solution of ammonium acetate;
 - leaching solution flow rate of 100 cm³/min;
 - temperature of the leaching solution: 22 °C.
- It results a lead extraction at 71.35 %.

TRANSFERABILITY OF THE EXPERIMENTAL RESULTS

Tests were undertaken on the travertine slabs used as fittings of buildings at the University Campus of the University of Rome "La Sapienza." Core samples were taken to appraise the state of contamination of the material. The highest levels of contamination were found in materials set as fittings of the buildings at the entrance to the campus, where cars stand with their engines running before entering the Campus.

The images, obtained using a scanning transmission electron microscope (Hitachi 2500) in order to analyse the surface of the travertine samples, exhibited the presence of PbCl₂ as recorded in Figure 7. The appearance of the crystals generated in the experiment is similar to that found in situ, as evidence from Figure 8.

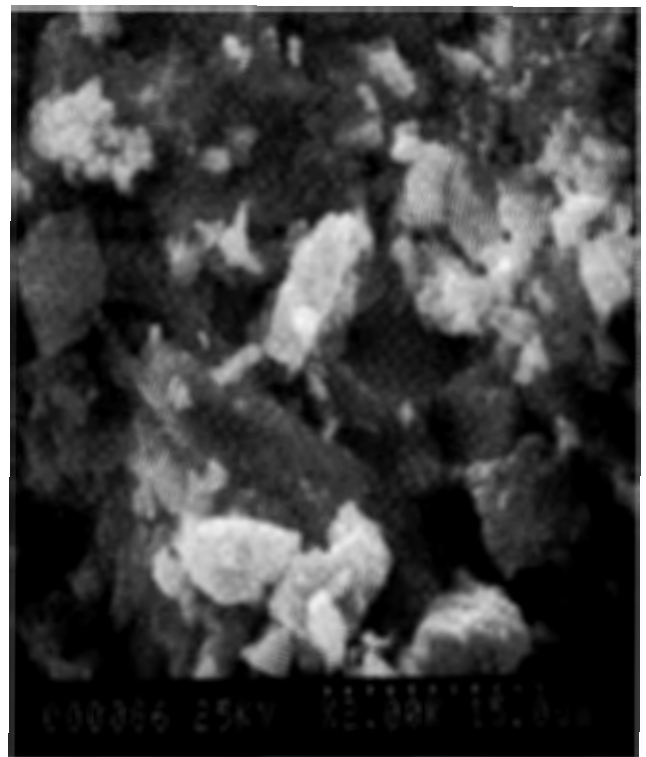


Figure 7. Image (x2000) of the surface of a sample of travertine taken from near the entrance to the Campus of the University of Rome "La Sapienza": the lead is identified by the particles at the centre of the image.



Figure 8. Image enlarged x2000 of the surface of a sample of artificially contaminated travertine: the lead is identified by the brighter particle at the centre of the image.

Lead maps of the lead related to the images 7 and 8 are recorded in Figure 9 and 10 for the particle revealed in the Campus and for the particle artificially generated respectively. The distribution of lead, the size and the shape of the two kind of particles are quite similar.

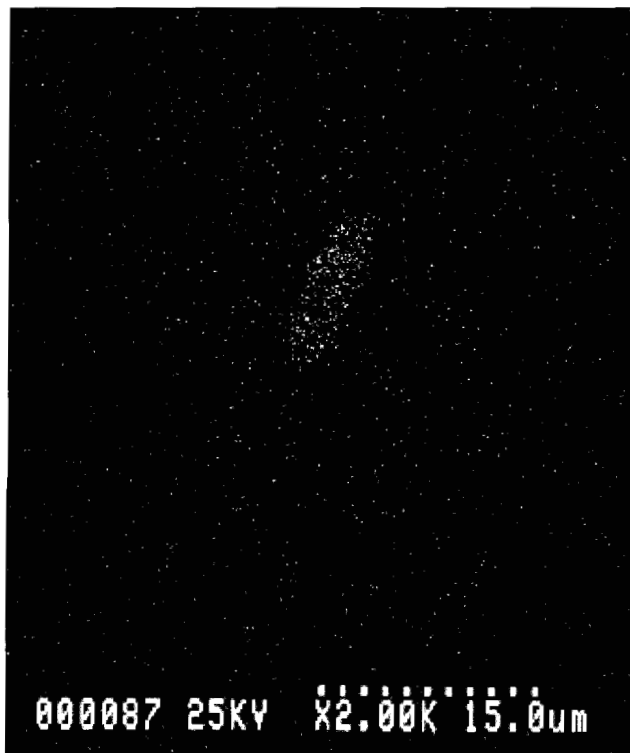


Figure 9. Map of the lead related to the image of the sample in Figure 7: the white dots clustered at the centre indicate the presence of lead.



Figure 10. Map of the lead related to the image of the sample in Figure 8: the white dots clustered at the centre indicate the presence of lead.

CONCLUSIONS

It has been proved that it is possible to effectively remove contaminating lead from travertine stones using ammonium acetate leaching solutions.

On slabs fitted on the outside of buildings, the leaching process can be carried out by applying wads soaked by the leaching solution.

It should be borne in mind that the lead present on the surface of outer fittings of buildings can be partially dispersed in the environment due to atmospheric activity. In fact lead compounds can be leached by rain, thereby percolating to contaminate the soil of flowerbeds, street dust and wastewater.

Due to the pervasiveness of the phenomenon it seems important to act with urgency to protect monumental buildings and the environment.

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