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Remediation of a Heavy Metals Contaminated Site with a Botanical Garden: Monitoring Results of the Application of an Advanced S/S Technique

Petra Scanferla*[a], Antonio Marcomini[b], Roberto Pellay[c], Pierandrea Girotto[c], Dino Zavan[c], Maurizio Fabris[c], Amilcare Collina[d]

[a]Consorzio Venezia Ricerche, via della Libertà 12, Marghera-Venice
[b]Dept. of Environmental Sciences, Informatics and Statistics, University Ca' Foscari, Dorsoduro 3246, Venice
[c]Mapintec srl, via Romea 8, Mira-Venice
[d]Mapei SpA, via Cafiero 22, Milan
sp.cvr@vegapark.ve.it

An innovative stabilization/solidification (S/S) technology called HPSS has been applied for the first time in a very delicate environment with a historical botanic garden in Venice for the remediation of a soil contaminated by heavy metals (As, Cu, Hg, Pb, Sb, Sn). This S/S technique, based on the High Performance Concrete (HPC) know-how (Scanferla et al., 2009), has been already successfully applied for the reconversion of different industrial contaminated sites into residential ones. The technology allows the remediation of contaminated soil fine fraction which is transformed into a very dense, low porous and mechanically-resistant granular material with the environmental characteristics for its reuse as filler in direct contact with the roots of the vegetal patrimony. More than 8,000 m^3 of contaminated soil fine fraction has been treated and monitored throughout 34 representative samples. Metal leachability was verified according to a leaching test method for granular waste (EN 12457-2, 2002) in which the demineralized water has been replaced with artificial sea water in accordance to Local Environmental Agency requirement. The mechanical properties were measured according to Los Angeles (LA) test method (BS EN 1097-2, 2010) for construction aggregates obtaining very good results in toughness and abrasion resistance. The granular material has been used tout court under the final floor layer in transit way and mixed with compost and soil in green areas also beside the rhizosphere horizon.

1. Introduction

Soils are the major sink for heavy metals released into the environment by many different anthropogenic activities and unlike organic contaminants which are oxidized to carbon oxide by microbial action or other type of natural attenuation, most metals do not undergo microbial or chemical degradation and their total concentration in soils persists for a long time after their introduction such as in the case of different filling material used in the past for the land raising of same part of Venice. The adequate protection and restoration of soil ecosystems contaminated by heavy metals require their remediation in relation to the risks and hazards posed by these contaminants to humans and the ecosystem (Wuana and Okieimen, 2011), even if the contamination takes its origin long time ago. Immobilization, soil washing, and phytoremediation techniques are frequently listed among the best demonstrated available technologies (BDATs) for remediation of heavy metal-contaminated sites.

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Solidification/stabilization (S/S) technologies, especially as in situ applications, are very common in the United States and are increasing in Europe (Harbottle et al., 2007). Among this type of remediation there is an innovative solidification/stabilization process (S/S) named HPSS based on the High Performance Concrete (HPC) know-how, which was developed for the remediation of a dismissed industrial site in Murano-Venice (Surico et al., 2003), an area highly contaminated in the past by heavy metals due to the uncontrolled discharges of wastes from artistic glass productions.
The HPSS process, covered by a European patent, has been already successfully applied for the reconversion of different industrial contaminated sites into residential ones (Scanferla et al., 2009). On the base of the monitoring results of the demonstration project completed in 2005 and its proved reliability, it has been accepted a project designed with the application of this technology for a dismissed electric power station with a broad park area. The main peculiarities of this technique are:

1) the addition of innovative additives to the soil finer fraction that allow high-performance soil stabilization levels obtained with around a 27 % of cement additive;
2) providing the stabilized soil with a granular form that can be easily managed, also in the case of maintenance work for underground pipelines.

This paper reports the results of the monitoring program of physico-chemical and mechanical properties of by-products generated and used as filling material in an area with an important plants patrimony. However the results of the germination and growth tests are not reported. Nevertheless these tests performed before the project approval to evaluate differences in growth rate of a soil with high percentage of HPSS granular material (up to 50 % in volume) shown any significant alterations.

2. The case study

The contaminated area of about 18,500 m^2 is located in a historic part of Venice, in which there are six main buildings (of about 8,500 m^2) used in the past for many different activities as part of an electric power station operating until 1997 and one of the biggest park of Venice (of about 7,000 m^2), which was in the past a botanical garden inaugurated in 1847, not cured from the 1950s.
In 2003, after the end of the industrial activities, it was decided to transform the site in a residential area but the high contamination of the soil required the implementation of the soil remediation.
The contamination was not only caused by the industrial activity but it had its origins also from the type of soil and industrial wastes used in a distant past as filler material to raise this part of the island. So the contamination, consisted mainly of heavy metals was found also in the park area. The average level of the contamination is reported in Table 1, in which the mean values of concentration of the inorganic contaminants on the fine fraction of the soil samples are compared with the limits for the residential and the industrial uses in Italy (IMD, 2006) and with the risk based acceptable concentrations. The risk analysis evaluation came out the exposition to the contamination of the soil of the first meter was not tolerable.

Table 1: Concentration of the heavy metals of concern in the soil fine fraction

Heavy metals	Maximum soil concentrations	Mean soil concentrations	Risk based acceptable concentration**	Residential use limits***	Commercial /industrial use limits***
As (mg kg-1 dm*)	**35.2**	21.2	**0.26**	20	50
Cu (mg kg-1 dm*)	**1,559**	438	**160**	120	500
Hg (mg kg-1 dm*)	**17.02**	5.4	**0.02**	1	5
Pb (mg kg-1 dm*)	**2,129**	593	**260**	100	1000
Sb (mg kg-1 dm*)	**24.4**	11.3	**7.0**	10	30
Sn (mg kg-1 dm*)	**118.5**	45.2	**7.0**	1	350

*soil dry **risk threshold level calculated by site specific risk assessment ***(IMD, 2006)

After different pilot tests and a fairly long authorization project procedure for the evaluation of the HPSS application, was approved a remediation project with an plant *on site* designed to treat about 60 m^3/d. The plant was composed of a series of operating units similar to those indicated by Scanferla et al.

(2009). First of all, the contaminated soil was excavated preserving the rhizosphere areas which were removed as much as possible by means of a high pressure washing and collecting system. The excavated soil was screened if necessary. The coarse fraction (CF) (Ø > 4 mm) was mainly composed of brick, concrete and stone debris, and could be grind in a mill or send to a recycling authorized plant out of the site after a washing procedure. Conversely, the highly polluted fine fraction (FF) (Ø ≤ 4 mm), mainly composed of silt and clay, was considered for S/S treatment. The proposed S/S technique was designed to produce stabilized material in granular form by mixing contaminated soil (FF) with Portland cement, water and a specific additive (SA) called Mapeplast ECO1 with water-reducers and waterproofing agents. A typical formulation is: 65 % – 70 % of FF, 23 % – 27 % of Portland Cement (CEM I 52.5 R), 2 % of the SA and 3 % – 5 % of water. The specific additive is adjoined to the mixture to improve S/S performance on the basis of the High-Performance Concrete (HPC) approach, allowing the water/cement ratio (W/C) to be strongly reduced respect the traditional S/S technique and enhancing the ability to support stabilized long-term mechanical soil properties, increasing density, lowering leachability and prolonging its life in severe conditions (Scanferla et al., 2009). The mixture is granulated via a rolling plate system. The grain specific surface area and its corresponding diameter, that is maintained in the range 20 mm – 100 mm, is controlled by changing the process parameters. After 28 days curing in a storage area dedicated to allow cement hydration, the stabilized material is deemed as ready to be replaced *in situ*. The filling materials section was different depending on the final destination of the area (pedestrian or green zone) as shown in Figure 1.

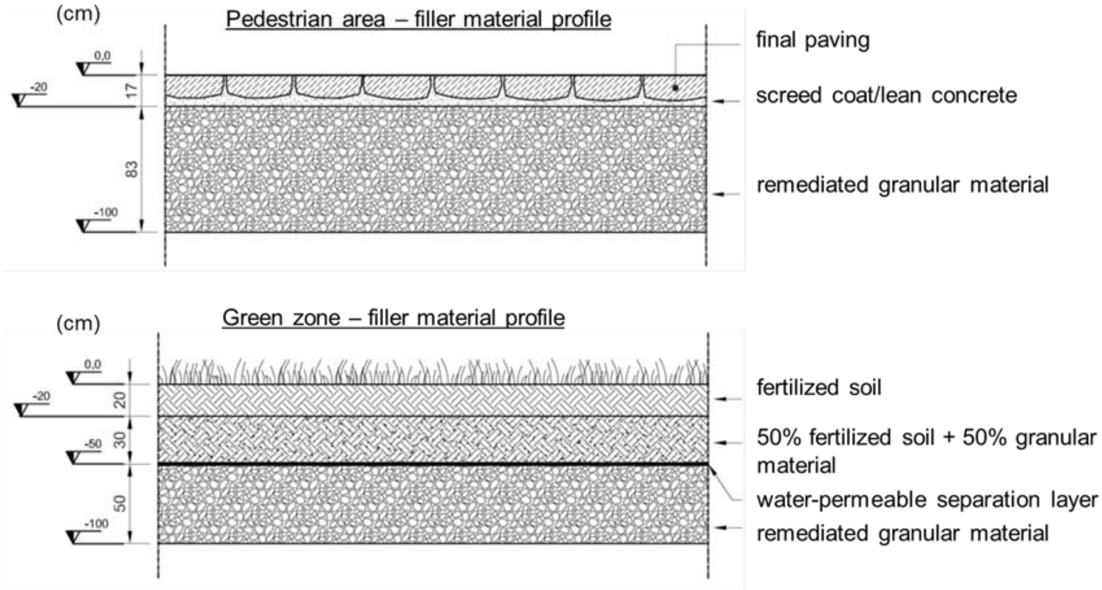

Figure 1: Filler material sections

3. Materials and methods

3.1 Sampling and sample preparation

A total of around 8,000 m^3 of polluted soil has been treated, resulting in about the same volume of granular material totally reused in site. During the S/S treatment, samples were collected of the FF before the treatment and of the stabilized grains (G), which were tested after 28 days of curing to allow the cement hydration process, resulting in 68 final composite samples (from FF1 to FF34 and from G1 to G34). In order to perform a more detailed control at the beginning of the remediation activities each of the first 10 samples were representative of lots of around 100 m^3 of stabilized grains, the other 24 samples were representative of lots of around 300 m^3. The sampling was realized in according to EN 12457-2 (2002).

3.2 Leaching test and physico-chemical analysis

The assessment of sample leachability was evaluated by a leaching protocol according to the EN 12457-2 (2002) procedure concerted with the local environmental authority (ARPAV): the samples were leached before and after treatment with deionized water (24 h, S/L = 1:20) amended with $MgSO_4$ (10 g L^{-1}) under mechanical agitation. This test was specifically designed adding sulphates to the eluent which represent one of the most relevant cement aggressive agent, which are present in lagoon water, in order to make the test more harsh and pertaining to the site specific conditions. The pH was measured using a pHmeter HI 9025 Microcomputer from HANNA Instrument®. As (Limit of Detection (LOD) = 0.5 µg L^{-1}, p=0.01), Cu (LOD = 10 µg L^{-1}, p=1), Hg (LOD = 0.5 µg L^{-1}, p=0.05), Pb (LOD = 1 µg L^{-1}, p=0.01), Sb (LOD = 0.5 µg L^{-1}, p=0.01) and Sn (LOD = 0.5 µg L^{-1}, p=0.01), were detected via Inductively Coupled Plasma Atomic Optical Emission Spectroscopy (ICP-OES) (Spectro Flame Compact E, Analytical Instruments).

3.3 Mechanical test

The mechanical characteristics were verified after curing to prove the granular material suitability as filler by a Los Angeles (L.A.) test (BS EN 1097-2, 2010). The L.A. test applied to natural, manufactured or recycled aggregates used in building and civil engineering, measures of degradation of mineral aggregates of standard grading resulting from a combination of actions including abrasion or attrition, impact and grinding in a rotating steel drum containing a specified number of steel spheres. The L.A. Abrasion test is widely used as an indicator of the relative quality or competence of aggregates and represents the weight percentage ratio between the crushed material fraction after the tests application and its initial amount before the test start. The lower L.A. value the higher the mechanical characteristics of aggregated material. This test provides a quantitative method for evaluating the quality of aggregates for use in highway construction.

4. Results

4.1 Leaching data

The average values of chemicals (As, Hg, Cu, Pb, Sb and Sn) originating from the survey area and reported in Table 1 showed that all considered metalloid and metal concentrations exceeded the relative Italian standard for soil residential use (IMD, 2006) such as the risk based acceptable concentrations. Chemical analyses on leachates generated before and after treatment according to method reported are displayed in graphs in Figure 2 for Sb, As, Cu. The results of Pb, Hg and Sn are not reported in graph because all the leaching after treatment presented a concentration under the detection limit as happened for Arsenic in different treated samples. Data highlighted that the leaching concentration strongly decrease respect that obtained from the original soil (FF) and is below the limit take as reference, the acceptable concentration for groundwater (IMD, 2006) with high level of reduction. The percentages reduction for each contaminant are shown in Table 2. The leaching of copper was quite under the limit also for fine fraction before the treatment but the reduction is as well remarkable (75 % ± 11 %). These results, in relation also to the more restrictive threshold limits take into account respect to those used in for the waste recycling into environment (IMD, 1998), confirmed the curing effects of the devised S/S process and the substantial immobilization of metalloids and metals. Furthermore beside the displayed results, the monitoring had taken into consideration also other relevant heavy metals as Cr(VI) and Al which have to be necessary consider when a S/S has implemented. All the 21 heavy metal concentrations of the 34 eluates analysed were under the limit values considered (groundwater acceptable limit, IMD 2006).

Another important parameter which need to be taken into account for the plants health in the presented case study, is the final pH of leaching of the granular material and the pH level after its use as filler material. The pH of the leaching was always under 9.76 and over 7.76 (mean value 8.8 ± 0.7; n=34), very low values considering the Portland use and considering the limit of 12 required for soil recycling in environment (IMD, 1998). This pH is further lower for the granular material in site thanks to the buffering capacity of the soil mixed to the S/S aggregates obtained with the S/S remediation. The pH of the layer (see Figure 1) with 50 % of new fertilized soil and 50 % of granular material is around 7.3 (mean value 7.3 ± 1.1; n=10) similar to the pH of the soil before the remediation that was around 8.6.

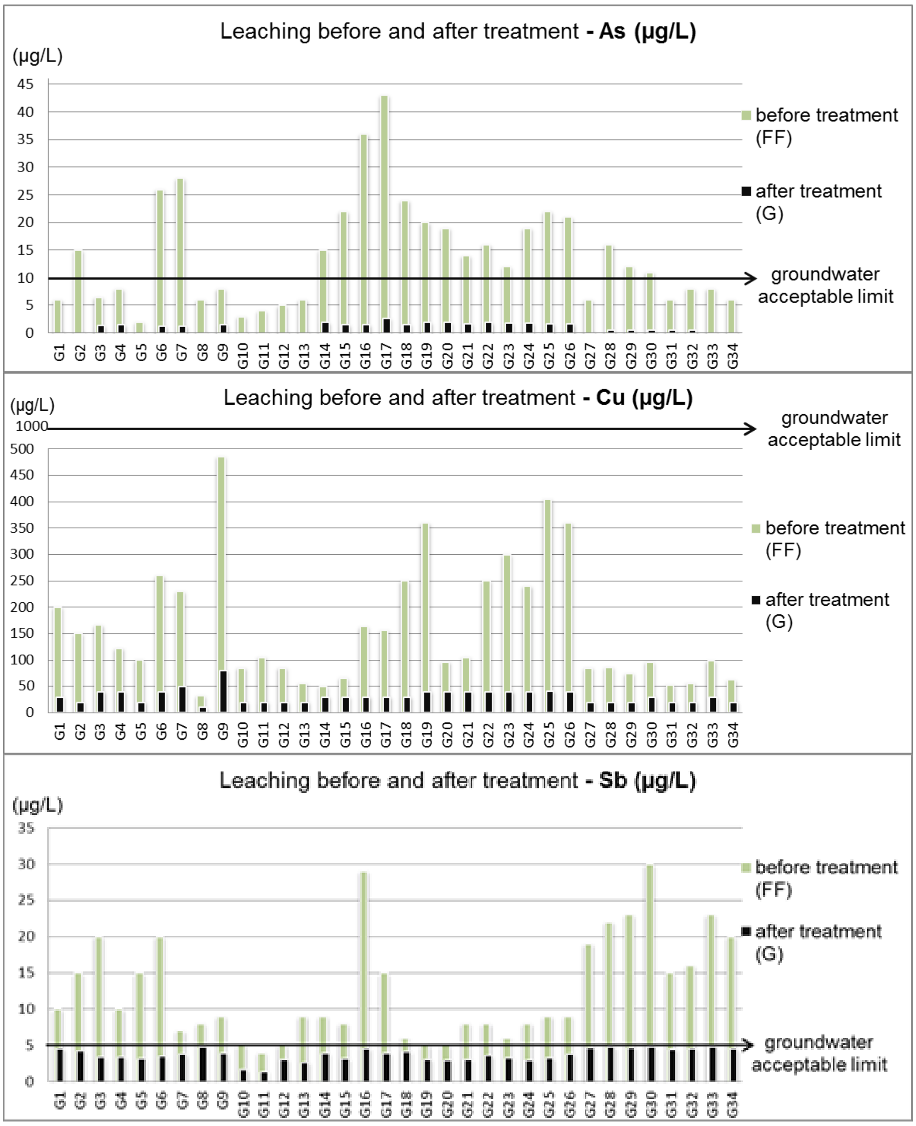

Figure 2: Comparison of As, Cu and Sb concentrations in the leachate before and after treatment.

Table 2: Reduction of heavy metals leaching after the treatment

Heavy Metals	% of reduction in leaching concentration ± s.d.	Maximum % of reduction	minimum % of reduction
As	91 ± 5	98	78
Cu	75 ± 11	90	40
Hg*	93 ± 3	99	89
Pb*	89 ± 7	95	80
Sb	63 ± 15	84	30
Sn*	80 ± 2	82	50

4.2 Mechanical data

Concerning mechanical properties, the samples presented an average L.A. = 34.8 % ± 1.1 % (n=34), which is very low and stays in the range of the granite rocks (27 % - 49 %), (Smith and Collins., 2001).

The Italian classification for unbound material used in road construction in according to EN 13242 (2002), BS EN 13285 (2010) and ASTM D3282 (2009), which specify the properties for hydraulically bound and unbound materials as well as aggregates of recycled materials for civil engineering work and road construction, indicates that an aggregated need to have a L.A. loss < 40 % for its use in urban roadway.

5. Conclusions

The combination of sieved contaminated soil, cement and specific HPC additives, properly mixed and converted to granular material, showed not only low leachability rates, but also high durability performance. The projection of the leaching of the contaminated soil stabilized using this S/S technique over a 100-year period has already been reported by Surico et al. (2003) and indicates that the cumulative leaching is far below the limits stated in the Dutch Building Material Decree. However, a long-term monitoring plan over several years is currently running in order to monitor the aggregates leaching and durability. Three monitoring piezometers installed in site will allow any change in leachate characteristics to be checked, tracing the effectiveness of the considered remediation procedure on a long-term basis. The case study is mainly of interest in relation to the environmental context of the application because the S/S material has been used as filler material mixed with fertilized soil close to rhizosphere of an important vegetal patrimony (with speciemen of *Platanus orientalis* L. and *Quercus ilex* L. trees with trunks around five metres round) without plant heath significant alterations which are constantly monitored.

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