

In situ remediation of polluted Spolic Technosols using Ca(OH)₂ and smectitic marlstone



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ABSTRACT

Technosols are soils developed on non-traditional substrates and containing large quantities of materials mostly due to intensive human industrial activity, such as artefacts. The increasing number of sites affected by Technosols and their impact on the environment as growing media for plants or as source of pollutants require an understanding of their functioning and evolution, above all the knowledge on the transport of toxic substances from contaminated technogenic soils to groundwater. A case study on properties, remediation and evaluation of Technosols made up by vitrified fly ash and glass–ceramics in Italy was carried out. Original technogenic soils, classified as Spolic Technosols (ecotoxic), were pedotechnically *in situ* remediated by adding smectitic marlstone and Ca(OH)₂. Chemical analysis on samples from piezometers showed the presence of harmful heavy metals in groundwater. By means of boreholes and soil profiles the new soils generated, after remediation, were physically and chemically characterized and classified as Spolic Technosols (calcaric). Analysis on soil toxicity and leaching tests showed the effectiveness of the remediation and the mobility reduction of some potentially harmful elements according to the environmental Italian regulation.

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1. Introduction

Soils have been significantly altered by humans (Dudal, 2004) so that their characteristics seldom resemble the native or agricultural soils (Dazzi and Monteleone, 2007; Hartley et al., 2008). Man's activity in agriculture, urban, industrial, traffic, mining and military areas (SUITMA Wiki page, 2013), induces soil modification and degradation through physical, chemical and biological transformations but also creates new soils characterized by the presence in various proportions of pedological, lithological and technogenic materials (Bryant and Galbraith, 2003). Soils that have been profoundly modified by addition of organic materials or household wastes, irrigation and cultivation are now referenced as Anthrosols. Soils developed on non-traditional substrates or containing large quantities of materials mostly due to intensive human industrial activity, such as artefacts, are now referenced as Technosols.

These last, in particular, in the World Reference Base for Soil Resources (IUSS Working Group WRB, 2007) are a new Reference Soil Group that “combines soils whose properties and pedogenesis are dominated by their technical origin” and include, among others, soils derived from “non-traditional pedomaterials” originated from human activities. Generally speaking, Technosols are characterized by extreme

values of bulk density (from less than 0.5 to more than 1.6 kg dm⁻³), coarse textures, great both horizontal as well as vertical heterogeneity (Lehmann and Stahr, 2007; Morel et al., 2005). These man-made soils should fulfill the main soil functions as defined by the EC-COM 231/2006 (European Union, 2006) and hence should represent an environmentally sound mixture (e.g., low pollutant availability, low ecotoxicity).

As Camps Arbustain et al. (2008) stressed the preparation of Technosols from mixtures of unconsolidated wastes, e.g., sludges and fly ash, may be an important and feasible method of re-using waste products and restoring degraded areas, while at the same time recycling essential nutrients and stabilizing the organic matter present in such materials. However, the positive functions of newly prepared soils do not guarantee that the contaminants will be stored safely and indefinitely (Yao et al., 2009). Environmental problems resulting from the use of these mixtures could be avoided if the characteristics of the materials employed were well known and adequate for such purposes (Camps Arbustain et al., 2008). The increasing number of sites affected by Technosols and their impact on the environment as growing media for plants or as source of pollutants require an understanding of their functioning and evolution (Monserie et al., 2009). Various authors have reported increases in the concentrations of heavy metals in leachates after the application of biosolids to soils, although their mobility was highly influenced by pH, as well as some other properties. Camps Arbustain et al. (2008) in particular, investigating the extractability

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and leachability of heavy metals in tailor-made Technosols, highlighted the existence of complex interactions among organic matter solubility, pH and heavy metal extractability.

Technosols tailored with fly ashes produced by municipal solid waste incinerators (MSWI), result in a number of changes in the adjacent ecosystems as toxic substances are leached out and transported to the soil and groundwater (Haynes, 2009). Ash from MSWI is a heterogeneous mixture of slag, metals, ceramics, glass, other non-combustible materials and unburned organic materials (Cheeseman et al., 2003; Li et al., 2007) and constitutes a real hazard for environmental health and human safety because of the high levels of metals such as Pb, Cu, Cr, Ni, and Cd (Shim et al., 2005).

Vitrification is a thermal method of pedotechnique that can reduce the volume of waste by 60% or more and that allows for incorporating metals into the amorphous structure of glass, which is a more resistant product to leaching than the primary material. Furthermore vitrified materials are more environmentally stable for reuse or production applications such as secondary raw materials (Lam et al., 2010). The term pedotechnique (Fanning and Balluff Fanning, 1989), indicates all those anthropogenic activities, that since 1980 have seen a growing influence of man on pedogenesis and on soils (as for example in agriculture management, or for waste disposal, or in mining operations, etc.), both by the selection and evaluation of suitable materials for the “construction” of soils, or by the use of appropriate procedures to modify the characteristics of the soil, till the construction of soils for specific purposes, such as happens in large scale farming (Dazzi and Monteleone, 2007; Dazzi et al., 2009; Lo Papa et al., 2011).

In order to secure the environment from leaching of heavy metals from the treated materials, various leaching tests have been developed to determine the interaction of waste with the surrounding environment and several surveys have been published on the vitrification of solid waste (Haugsten and Gustavson, 2000; Lam et al., 2010; Park and Heo, 2004; Romero et al., 1999) using pedotechnique methods that have also highlighted the drawbacks.

Following such considerations and results, for the purpose of improving the use of pedotechnique methods in the solidification/stabilization of partially vitrified fly ash and glass–ceramic (VFA), a survey was planned aiming at: i) estimating the VFA characteristics and the environmental hazard 28 years after being abandoned in a landfill; ii) assessing the possibility of in situ remediation of this waste with $\text{Ca}(\text{OH})_2$ and smectitic marlstone and iii) classifying the Technosols before and after the pedotechnique treatments.

2. Materials and methods

2.1. Study area

The study area is located in the Municipality of Castenaso (Emilia Romagna Region, Italy; Fig. 1a) over an alluvial terrace characterized by Haplic Fluvisols, a flat morphology, an average altitude of 53 m a.s.l. and a continental climate (annual average temperature 13.3 °C; annual average rainfall 709 mm).

It is represented by an old kiln, 24,000 m² wide and with a nearly rectangular shape that in 1979 was landfilled with partially vitrified fly ash and glass–ceramic (VFA) waste which, straight after, was covered by an earthly material that is to be considered as a human transported material (HTM) according to ICOMANTH (2003). As emerged during the field survey, the HTM layer was around 20 cm thick, with a volume of about 3500 m³; the layer of waste was 20/130 cm thick, with a volume of about 17,000 m³. This last was followed in sequence by (Fig. 2): a subsoil (SS); a silty clay loam layer (SCL) and a sandy loam layer (SL). The human-derived artifacts in SS discriminate this layer from SCL.

2.2. Field survey and remediation treatment procedure

The field survey started in 2007 along three parallel transects (a–a', b–b', c–c') with a NE–SW direction in order to cover the whole study area (Fig. 1b).

As the aim of the work was to investigate the features of the tailored soils and of the natural substrata, we opened eighth soil profiles up to 2 m deep (E in Fig. 1b); while ten boreholes (D in Fig. 1b) 6 cm \varnothing and up to 5 m deep were made.

On the whole, we got 82 samples: 18 from HTM; 18 from VFA; 18 from SS; 18 from SCL; 10 from SL. Samples from each horizon of the eight soil profiles, corresponding to HTM, VFA and SS layers, were collected within a vertical depth of 5 cm from the upper and lower horizon boundaries, while SCL and SL were sampled by means of boreholes. Soil samples were milled, sieved and homogenised.

Four piezometers with a diameter of 10 cm and till a depth of 4 m, were placed using a drill in order to determine the risk of leaching of trace elements from VFA into the groundwater (Fig. 1b).

The in situ remediation treatment was carried out in five selected sites (T in Fig. 1c). A known volume of VFA was mechanically sampled (digging holes of 300 cm \varnothing and 70 cm deep) weighted and then

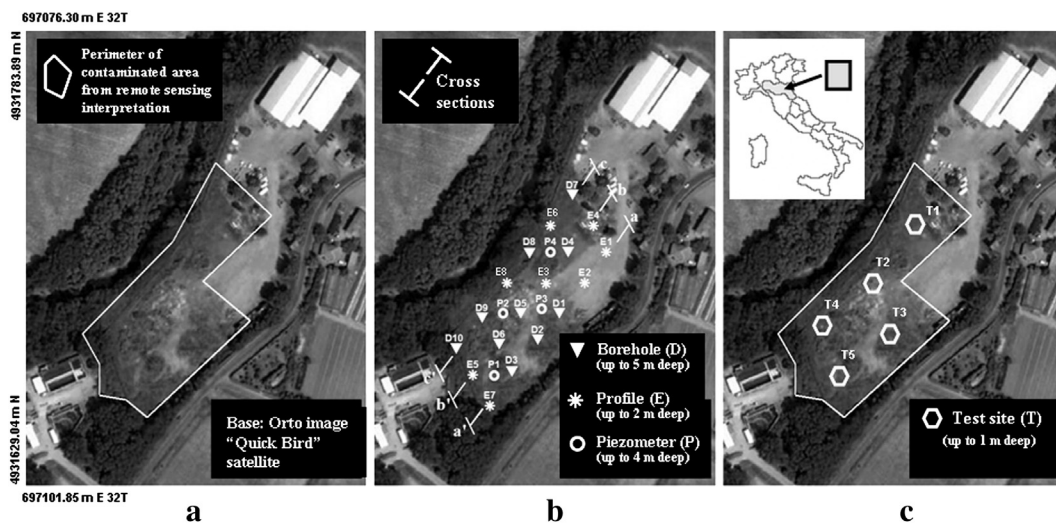


Fig. 1. a) Quick Bird satellite image with delineation of the study area. The image was obtained by overlap of 0.7–1.0 nm (red-infrared) and 1.1–1.5 nm (infrared) spectral bands. Spectral image analysis showed that 1.0 and 0.7 nm absorption bands, typical of solid materials rich in oxide and hydroxide metals, characterize the study area with different grey levels from the surrounding area. b) Location of boreholes, soil profiles and piezometers. c) Location of test sites.

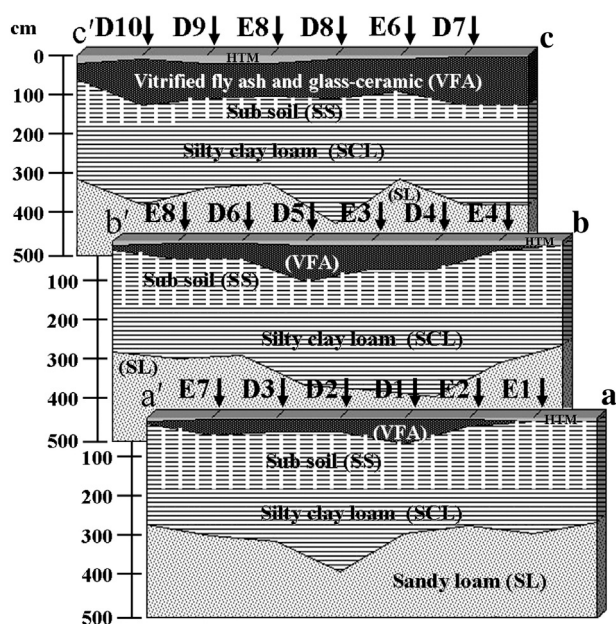


Fig. 2. Stratigraphic reconstruction of the cross sections with boreholes (D) and soil profiles (E) location.

mixed with $\text{Ca}(\text{OH})_2$ and smectitic marlstone (VFA/CAM) at a w/w ratio of 20% and 5% respectively. After one year the VFA/CAMs were sampled and analysed. The marlstone used for VFA treatment belongs to the “Monghidoro” lithological Formation which is made by 30% of carbonates and 70% of clay minerals. Its mineralogical composition after decarbonation and in decreasing order of abundance shows: 76% smectite, 5% chlorite, 4% plagioclase, 3% quartz and kaolinite, 2% K-feldspar and mica. Table 1 shows the total contents of trace elements of such marlstone after AR digestion.

Multitemporal aerial images (VololItaly2000) and the spectral study of satellite images (Quick Bird satellite) were used to characterize the study area by the adsorption bands.

2.3. Laboratory analysis

All the samples collected from the field survey were firstly 2 mm sieved and then fine pulverized, homogenized and analysed. 250 mg from each homogenized and powdered sample was digested with Aqua Regia (HCl/HNO_3 3:1) in a micro-wave oven (Milestone 1200) in Teflon vessels, according to Vittori Antisari et al. (2011). The solutions were analyzed for major and trace elements using a Spectro Inductively Coupled Plasma Optical Emission Spectrometer (Circular Optical System CIR.O.S.^{CCD}). To obtain the calibration lines, certified multi elements standard solutions were used (CPI International, Amsterdam). The accuracy of the analytical method was tested by analysing certified standard specimens of soil (BCR-CRM 141R, 142R, 143R). A composite sample of 10 kg of VFA, collected from 18 sites (D and E in Fig. 1b), was dried at room temperature and split into quarters. In each quarter, the skeletal fraction ($\phi > 2$ mm) was determined (w/w). The fraction ≤ 2 mm ϕ was composed of two different matrices distinguishable by their different colours: a grey one (10YR 5/1) and a reddish-brown one (5YR 5/4).

Table 1

Trace elements in the smectitic marlstone used for VFA treatment. Values are in mg kg^{-1} (DL = detection limit).

| As | B | Cd | Co | Cr | Cu | Li | Mo | Ni | Pb | Sb | Sn | V | Zn |
|-----|------|-----|-----|------|------|------|-----|------|-----|-----|-----|------|------|
| 4.8 | 67.1 | 0.4 | 7.2 | 68.3 | 19.9 | 27.6 | 0.7 | 34.9 | <DL | <DL | <DL | 73.8 | 59.9 |

Samples from the reddish brown and the grey matrix were homogenized separately in an agate mortar. Chemical determinations were obtained by X-ray fluorescence spectrometry (XRF) (Philips PW 1480) on pressed powder pellets, following the matrix correction methods (Franzini et al., 1975; Leoni and Saitta, 1976). The estimated precision and accuracy for trace-element determinations were better than 5%, except for those elements < 10 ppm (10%–15%). LOI (Loss on Ignition) was evaluated after overnight heating at 950°C . International reference materials were used in the calibration and as analytical monitor. In addition, 250 mg of each coloured matrix was mineralized with Aqua Regia as described above.

2.4. Leaching test

After one year by remediation treatment, VFA and VFA/CAM were sampled and leaching tests (UNI EN 12457-21 method), in compliance with the Italian laws (D.M. 186/2006), were performed in triplicate. Briefly, one hundred grams of undisturbed samples, both treated and untreated, was weighted and added with 500 mL of deionized water (Milli Q). After 2, 8, 24, 48, 72, 102, 168 and 384 h (Decreto Ministeriale n.186, 2006) from each sample 20 mL of supernatants was collected and analysed for pH (Crison pH-meter), electrical conductivity (EC at constant temperature $20 \pm 1^\circ\text{C}$), and trace elements. An aliquot of these water samples was filtered with Whatman 42 filter, then acidified with HNO_3 1 M (HNO_3 65% suprapuro, Merck). Samples were analysed by ICP-OES, while the accuracy of the analytical method was verified by analysing certified standard specimens of water (CRM 609-Community Bureaux of Reference, BCR).

The groundwater was sampled every 2 weeks and the piezometer level was recorded. Water samples were analyzed using an Inductively Coupled Plasma Optical Emission Spectrometer (Spectro, Circular Optical System CIR.O.S.CCD), according to Vittori Antisari et al. (2010).

3. Results and discussion

3.1. Characteristics of vitrified fly ash and glass-ceramic (VFA) waste

Among the 36 elements determined by Aqua Regia extraction and plasma spectrometry, only the results for As, Cd, Cr, Cu, Ni, Pb, V and Zn concentration in HTM, VFA, SS, SCL and SL are discussed (Table 2). The average concentration of trace elements in VFA was higher than those found in SS, SCL and SL and the Italian Law threshold (Decreto Legislativo n.152, 2006) for commercial and industrial use was exceeded for all elements with some exceptions. Vanadium concentration was less than the threshold for green and commercial use, while As, Cr and Ni amount was less than that for industrial use.

The concentration of trace elements in SCL and SL was low and very uniform between the two layers. The SS layer was affected by VFA waste deposited over, whereby the concentration of Cd, Cu, Pb and Zn was higher than the threshold for commercial use; for the remaining heavy metals the average value was very close. The VFA yielded toxic elements that were deposited in the SS layer. Until that moment, the danger of pollution of groundwater was averted because no heavy metals concentration was detected in water sampled by piezometers (data not shown).

The study of VFA composition showed that the deposit of waste ash was characterized by a coarse fraction (> 2 mm) composed by 28% of glass fragments and 18% glass-ceramic fragments and a fine fraction (54%) composed by two different matrices (37% of a reddish-brown matrix and 63% of a grey matrix).

The XRF analysis has provided the composition in oxides in the two matrices: the brown matrix is formed by Fe_2O_3 (58%), SiO_2 (16%), CaO (12%), and Al_2O_3 (7%) while the grey matrix by SiO_2 (47%), CaO (19%), Al_2O_3 (12%), Fe_2O_3 (8%).

The composition of municipal solid waste varies over time and from country to country, due to the differences in lifestyle and

Table 2
Statistic summary of trace elements concentrations in HTM, VFA, SS, SCL and SL layers obtained by Aqua Regia digest.

| Trace elements | Sample | Depth cm | Mean mg kg ⁻¹ | (Max–Min) | Standard deviation | Thresholds* | |
|----------------|--------|--------------|-----------------------------|-------------|--------------------|-------------|------|
| | | | | | | A | B |
| As | HTM | 0–30 | 4.5 | (5.2–3.6) | 0.6 | 20 | 50 |
| | VFA | 30–40/130 | 23 | (35–18) | 7.0 | | |
| | SS | 40/130–165 | 2.5 | (3.1–2.2) | 0.8 | | |
| | SCL | 165–270/400 | 0.60 | (0.61–0.58) | – | | |
| | SL | 270/400–500+ | 0.60 | (0.62–0.59) | – | | |
| Cd | HTM | 0–30 | 0.30 | (0.70–0.13) | 0.2 | 2 | 15 |
| | VFA | 30–40/130 | 37 | (45–30) | 5.6 | | |
| | SS | 40/130–165 | 16 | (27–10) | 3.3 | | |
| | SCL | 165–270/400 | 1.2 | (1.6–1.0) | 0.2 | | |
| | SL | 270/400–500+ | 1.0 | (1.3–0.9) | 0.1 | | |
| Cr | HTM | 0–30 | 56 | (65–43) | 8.2 | 150 | 800 |
| | VFA | 30–40/130 | 249 | (299–203) | 43.0 | | |
| | SS | 40/130–165 | 107 | (116–97) | 18.4 | | |
| | SCL | 165–270/400 | 32 | (47–28) | 5.2 | | |
| | SL | 270/400–500+ | 24 | (27–21) | 2.1 | | |
| Cu | HTM | 0–30 | 31 | (53–17) | 13.9 | 120 | 600 |
| | VFA | 30–40/130 | 1822 | (2172–1622) | 249.1 | | |
| | SS | 40/130–165 | 323 | (328–317) | 28.2 | | |
| | SCL | 165–270/400 | 23 | (28–17) | 4.0 | | |
| | SL | 270/400–500+ | 22 | (29–17) | 4.0 | | |
| Ni | HTM | 0–30 | 41 | (47–30) | 6.7 | 120 | 500 |
| | VFA | 30–40/130 | 191 | (246–146) | 43.2 | | |
| | SS | 40/130–165 | 92 | (97–85) | 5.0 | | |
| | SCL | 165–270/400 | 55 | (71–35) | 12.1 | | |
| | SL | 270/400–500+ | 58 | (68–48) | 6.9 | | |
| Pb | HTM | 0–30 | 23 | (31–16) | 5.6 | 100 | 1000 |
| | VFA | 30–40/130 | 3821 | (7444–2528) | 2042 | | |
| | SS | 40/130–165 | 112 | (129–93) | 33.6 | | |
| | SCL | 165–270/400 | 18 | (25–13) | 4.4 | | |
| | SL | 270/400–500+ | 17 | (35–11) | 7.0 | | |
| V | HTM | 0–30 | 39 | (49–28) | 8.3 | 90 | 250 |
| | VFA | 30–40/130 | 81 | (146–50) | 38.6 | | |
| | SS | 40/130–165 | 39 | (48–27) | 9.4 | | |
| | SCL | 165–270/400 | 38 | (49–27) | 9.6 | | |
| | SL | 270/400–500+ | 38 | (49–27) | 9.3 | | |
| Zn | HTM | 0–30 | 67 | (88–42) | 18.2 | 150 | 1500 |
| | VFA | 30–40/130 | 5726 | (7280–4828) | 954.0 | | |
| | SS | 40/130–165 | 271 | (285–263) | 10.3 | | |
| | SCL | 165–270/400 | 58 | (59–57) | 1.5 | | |
| | SL | 270/400–500+ | 46 | (57–40) | 7.0 | | |

* The Italian Law thresholds for urban parks and residential use (A) and for commercial and industrial use (B) were reported.

waste recycling processes of a country; the ash content also varies. Generally, the chemical and physical characterization of ash depends on the compositions of the raw MSWI, the operational conditions, the type of incinerator and air pollution control system design (Lam et al., 2010). The chemical composition showed that the major elements were Si, Al, Fe, Mg, Ca, K, Na and Cl, whereas, SiO₂, Al₂O₃, CaO, Fe₂O₃, Na₂O, K₂O are the common oxides found in

ash (Alba et al., 1997; Yang et al., 2009) it is reasonable to suppose that the different composition of the matrices can be due to the use of different additives during the activity of the incinerator plant (Garcia-Valles et al., 2007). The difference in composition was also reflected in the different concentration of trace elements incorporated into both amorphous and crystalline phases (Table 3). The solubilisation of silicate, oxides and hydroxides with AR method

Table 3
Min, max and mean concentrations of trace elements in fly ashes of MSW incineration from literature, mean concentrations in both matrices determined by XRF and AR-digestion methods, expressed in mg kg⁻¹, and percentage of extraction due to the ratio between XRF and aqua regia (AR-digestion).

| Elements | Concentration* | | | Reddish brown matrix | | | Grey matrix | | |
|----------|----------------|--------|--------|----------------------|--------------|--------------|-------------|--------------|--------------|
| | min | max | mean | XRF | AR-digestion | XRF/AR × 100 | XRF | AR-digestion | XRF/AR × 100 |
| | | | | mean | mean | % | mean | mean | % |
| As | 37 | 320 | 101 | 210 | 65 | 31 | 111 | 14 | 13 |
| Cd | 60 | 1000 | 130 | 18 | 13 | 72 | 31 | 10 | 32 |
| Cr | 200 | 3200 | 450 | 965 | 262 | 27 | 1943 | 460 | 24 |
| Cu | 960 | 2000 | 670 | 1333 | 1154 | 87 | 1827 | 1481 | 81 |
| Ni | 50 | 460 | 40 | 264 | 204 | 77 | 270 | 196 | 73 |
| Pb | 2400 | 54,000 | 3210 | 3993 | 1779 | 45 | 1400 | 1147 | 82 |
| V | 29 | 150 | 39 | 57 | 25 | 44 | 73 | 56 | 77 |
| Zn | 6200 | 55,000 | 10,390 | 4334 | 2442 | 56 | 3255 | 2302 | 71 |

* In fly ash composition from different MSW incinerators in Europe (Steiner, 2006).

Table 4

Statistic of trace elements (expressed as $\mu\text{g L}^{-1}$) in the leaching test of VFA and VFA/CAM after 1 year of incubation in situ. Leaching test was carried out according to the Italian Law. The As and Cd concentrations were not reported because their amount were lower than detection limit (DL). Σ is sum of trace elements concentration in the leaching water after 2, 8, 24, 48, 72, 102, 168 and 384 h.

| Trace elements | Sample | Mean Σ $\mu\text{g L}^{-1}$ | (Max Σ –Min Σ) | Standard deviation | Thresholds* $\mu\text{g L}^{-1}$ |
|----------------|---------|---------------------------------------|-------------------------------|--------------------|-------------------------------------|
| Cr | VFA | 201 | (312–129) | 76 | 50 |
| | VFA/CAM | 10 | (14–4) | 5 | |
| Cu | VFA | 770 | (1200–450) | 280 | 50 |
| | VFA/CAM | 656 | (821–147) | 455 | |
| Ni | VFA | 113 | (169–76) | 35 | 10 |
| | VFA/CAM | 9 | (11–6) | 2 | |
| Pb | VFA | 525 | (999–310) | 347 | 50 |
| | VFA/CAM | 28 | (72–11) | 39 | |
| V | VFA | 67 | (150–25) | 30 | 250 |
| | VFA/CAM | 40 | (47–34) | 6 | |
| Zn | VFA | 2020 | (2750–1200) | 571 | 3000 |
| | VFA/CAM | 121 | (183–48) | 68 | |

* Italian Law thresholds.

depends on the chemical form and bonds which characterized the compounds, and for this reason the different degrees of solubilisation can be due to the AR/XRF ratio (Bianchini et al., 2012). The solubility ratio in reddish-brown matrix decreased as follows: Cu (87%) > Ni, Cd

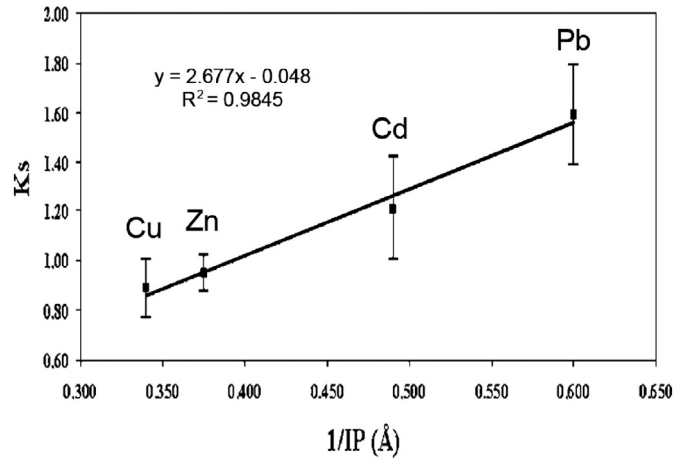


Fig. 4. Selectivity coefficient (K_s) of the soil clays, and ionic potential of some microelements (Cu, Zn, Cd and Pb).

(72%) > Zn > V, Pb (45%) > Cr, As (31%), whereas in the grey matrix: Cu and Pb (82%) > V, Zn, Ni (73%) > Cd (32%) > Cr, As (13%). The Cu compounds showed high solubility ratio in both matrices, while As and Cr compounds have low ratio, this changed in two matrices for Cd and Pb.

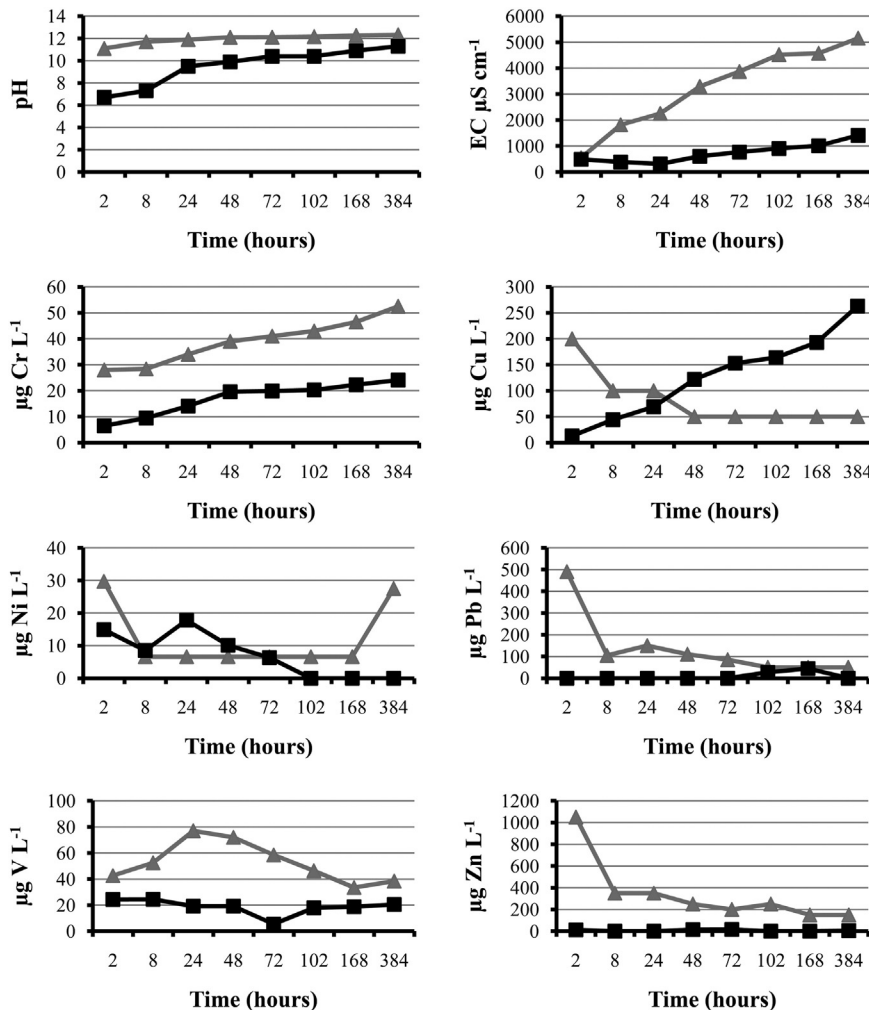


Fig. 3. pH, electrical conductivity (EC) and PTEs (Cr, Cu, Ni, Pb, V, Zn) behaviour of the VFA (grey triangle) and VFA/CAM (black square) during the 386 h of the leaching test.

3.2. *In situ* remediation of the VFA with $\text{Ca}(\text{OH})_2$ and smectite marlstone (VFA/CAM)

In situ remediation was carried out with a known volume of VFA treated with $\text{Ca}(\text{OH})_2$ and smectitic marlstone (VFA/CAM) at a weight/weight ratio of 20% and 5% respectively. After one year, the pollution hazard of waste treated with lime and marlstone (VFA/CAM) was compared with that untreated (VFA) to evaluate, through a leaching test, the trace elements released in water by both wastes treated and untreated (Decreto Ministeriale n.186, 2006). The As and Cd concentration in water samples for both samples was always lower than the detection limit and their values were not reported in Table 4. As expected, the hazard of pollution by VFA was high and the amount of Cr, Cu, Ni and Pb in water samples exceeded the Italian Law thresholds, while the treatment with lime and marlstone reduced the release of all trace elements with exception of Cu.

The treatment changes the bulk density of the sample and to allay that the results obtained can be due to the effect of dilution caused by addition of 25% CAM in weight of the sample treated a treatment with only $\text{Ca}(\text{OH})_2$ 25% was carried. Because of the release of pollutants from this last treatment, as expected, was much higher than the VFA (data not shown) it is possible assert that no effect was due to dilution of VFA materials.

The pH values for both VFA and VFA/CAM increased during the test ranging from 11.3 to 12.5 and from 6.8 to 11.5, respectively (Fig. 3); the same happened for the electrical conductivity (EC) values: the EC values in VFA reached 5 times higher than those in VFA/CAM. Metals are released over time without definite trends, therefore the hazard of VFA can be ascribed at high pH values found in water samples of the leaching test, whereas the metals solubility is controlled by the precipitation of insoluble minerals phases according to Eh-pH conditions (Alloway, 1992; Brookins, 1988; Takeno, 2005). The pH values ranging between 8 and 11 promote the precipitation of some metals as insoluble hydroxides (i.e. $\text{Cu}(\text{OH})_2$, $\text{Pb}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$), while pH values greater than 12 promote the dissociation of hydroxides (i.e. $\text{M}(\text{OH})_2 + \text{OH}^- \leftrightarrow \text{M}(\text{OH})_3^-$ or HMO_2). Cr, Ni and V contents increase in VFA leaching at pH higher than 11.5, while the dissociation of Cu, Pb and Zn does not occur yet.

Some amphoteric elements showed different solubilisation as a function of pH value at the solid–liquid interface (Johnson et al., 1996; Sanchez et al., 2000). In this case the hydroxides precipitate at pH 9 and become the predominant species at pH 11, conversely with pH value higher than 12 these hydroxides are soluble and high amount was found in water samples (Jing et al., 2004). Besides, the Zn excess

in solution causes oxidation–reduction processes with Cu(II) forming stable compounds with reduced Cu (Li and Wang, 2003).

The treatment with $\text{Ca}(\text{OH})_2$ and smectite marlstone used for the *in situ* remediation (VFA/CAM) maintains pH values lower than 11.5 favoring the stability of hydroxides, except for Cu. The carbonate fraction in smectitic marlstone may affect the lower risk of pollution than VFA in leaching test. This can be ascribed to the carbonate–carboxylic acid, forming new secondary carbonates with metals in solution such as PbCO_3 (cerussite), $\text{Pb}_3(\text{CO}_3)_3(\text{OH})_2$ (hydrocerussite), SrCO_3 (stronizianite) and $\text{Zn}(\text{OH})_6(\text{CO}_3)_2$ (hydrozincite), while the formation of $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ is very slow. Finally, the crystallographic property of smectite used for remediation has high both cationic selectivity degree and exchange capacity (CEC) that allow strong bonds with metals such as Pb, Cd, Cu, Zn (Ziper et al., 1988). These have a low both ionic potential and hydration energy whereby the bonds formed with superficial charge of clay minerals are very strong compared to ionic bonds. The degree of selectivity of different clay minerals (e.g. kaolinite, smectite, illite and montmorillonite) for metals can be calculated as a function of the cation's ionic potential and of the constant of selectivity (K_s) as proposed by Bolt and Bruggenwert (1976). The coefficient of selectivity (K_s) of smectite highlights a high affinity for Pb, significant for Cd, low for Zn and very low for Cu (Fig. 4). The characteristics of Pb allow a high absorption by marlstone smectite reaching the lowest concentration in the leaching water. This result is indicative of a favourable kinetic situation due to both adsorption capacity and secondary carbonate formation (Albuquerque and Labrincha, 2008; Bedelean et al., 2009; Ribeiro et al., 2008) and this order of affinity has been confirmed by studies of the adsorption rate and capacity of the smectite for the selected heavy metal ions from waste water of mines and other aquatic systems (Arpa et al., 2000; Traina and Doner, 1985; Wójtowicz and Stórkłosa, 2002). The difficulty to stabilise Cu also by VFA/CAM remediation lies in three main causes: i) the slowness of the Cu in forming carbonates; ii) Cu forms soluble hydroxide ions ($\text{Cu}(\text{OH})_4^{2-}$) in alkaline solutions because of its amphoteric behaviour and iii) the change of oxidation–reduction conditions that involve the Cu solubilisation in presence of Zn.

3.3. Consequences of land reclamation on soil features and classification

The comparison of multitemporal aerial images (VololItaly2000) coupled with the spectral study of satellite images (Quick Bird satellite) showed that the study area is characterized by two significant adsorption bands, respectively at 1.0 and 0.7 μm (Fig. 1a). The first is typical of iron (II) oxides, the second of iron (II) oxide and hydroxide. The

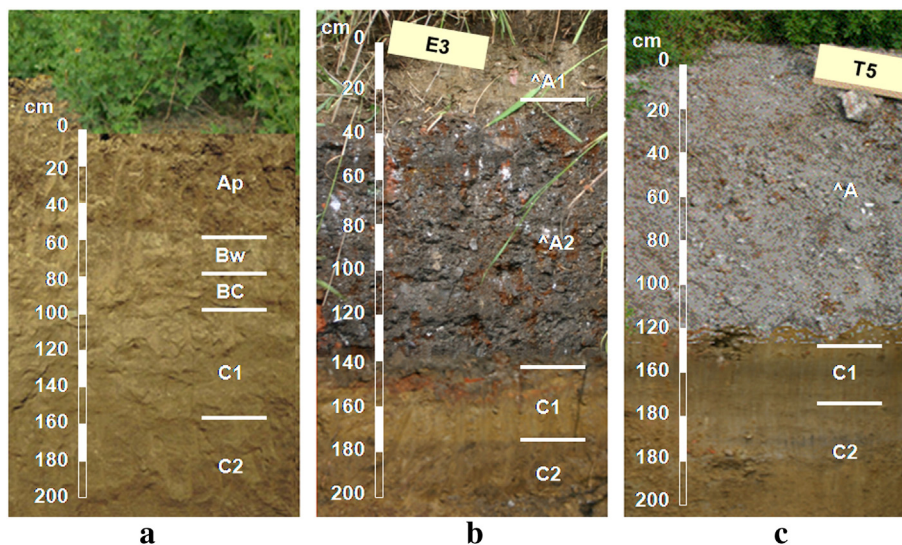


Fig. 5. Soil profiles of a) the original soils before the kiln installation, b) the soils of the landfill and c) the soils after the *in-situ* remediation.

Table 5
Field description of the pedons. The “caret” symbol (^) is used as a prefix to master horizon designations to indicate mineral or organic layers of human transported material.

| Pedon | Horizon | | Depth (cm) | Color/Munsell | | Structure ^c | | Roots ^d | | | Artifact (Human-derived) ^e | | | | |
|---------------------------|------------------------------|-----------------------|--------------|---------------|------------------|------------------------|----|--------------------|---|----|---------------------------------------|--------|----|---|----|
| | Master (layer ^f) | Boundary ^b | | D | T | G | S | T | Q | S | K | Q (v%) | R | P | S |
| | | | | | | | | | | | | | | | |
| Fluvisol Cambisol Siltic | Ap | A | 0–50/60 | S | 2.5Y 4/3 | 2 | m | sbk | 3 | vf | c | 3 | SR | N | IA |
| | Bw | C | 50/60–70 | S | 2.5Y 4/4 | 2 | m | sbk | 2 | f | a | 0 | | | |
| | BC | C | 70–95 | W | 2.5Y 4/4 | 1 | m | abk | 1 | f | a | 0 | | | |
| | C1 (SS) | C | 95–155 | S | 2.5Y 4/4 | 2 | m | abk | 1 | f | a | 0 | | | |
| Spolic Technosol Ecotoxic | C2 (SCL) | C | 155–200+ | S | 2.5Y 4/4 | 1 | co | abk | 0 | vf | a | 0 | | | |
| | ^A1 (HTM) | A | 0–20 | S | 2.5Y 4/3 | 1 | m | abk | 3 | fm | b | 9 | SA | N | IA |
| | ^A2 (VFA) | D | 20–40/130 | I | 10YR 5/1–5YR 5/4 | 3 | m | abk | 0 | f | fg | 46 | AN | P | NA |
| | C1 (SS) | G | 40/130–165 | S | 2.5Y 4/4 | 2 | m | abk | 1 | m | fg | 2 | SA | P | NA |
| Spolic Technosol Calcaric | C2 (SCL) | C | 165–270/400 | W | 2.5Y 4/4 | 2 | m | sbk | 0 | vf | a | 0 | | | |
| | 2C (SL) | U | 270/400–500+ | U | 2.5Y 5/5 | 1 | co | sbk | 0 | f | a | 0 | | | |
| | ^A | A | 0–120/130 | S | 10YR 6/1 | 3 | m | abk | 1 | a | fg | 38 | AN | P | IA |
| | C1 (SS) | G | 40/130–165 | S | 2.5Y 4/4 | 2 | m | abk | 1 | m | a | 0 | | | |
| | C2 (SCL) | C | 165–270/400 | W | 2.5Y 4/4 | 2 | m | sbk | 0 | vf | a | 0 | | | |

Corresponding layers of the boreholes^g.

Horizon Boundary^b: (D) Distinctness; A = abrupt, C = clear, G = gradual, D = diffuse; (T) Topography: S = smooth, W = wavy, I = irregular, U = unknown.

Structure^c: (G) Grade: 1 = weak, 2 = moderate, 3 = massive; (S) Size: m = medium; co = coarse; (T) Type: abk = angular blocky, sbk = subangular blocky.

Roots^d (Q) Quantity: a = absent, 0 = very few, 1 = few, 2 = common, 3 = many; (S) Size: vf = very fine, f = fine, m = medium.

Artifact materials^e (K) Kind: a = absent, b = brick, c = charcoal, f = fly ash, g = glass; (Q) Quantity: volume percent; (R) Roundness: AN = angular, SA = subangular, SR = subrounded; (P) Persistence: N = nonpersistent, P = persistent; (S) Safety: IA = innocuous artifacts, NA = noxious artifacts.

neighbouring areas show adsorption bands higher than 1.5 μm , typical for carbonates, silicates and non-metallic oxides (Clark et al., 2003, 2007). Such differences reflect the same differences of the soils that characterize the landfill study area and the surrounding areas.

The soils that originally (before the kiln installation) characterized the whole area (Fig. 5a), were strongly influenced by the alluvial substrata (due to the presence of the Idice river) and by the flat morphology. Such soils – Fluvisol Cambisol (siltic) according to the WRB (IUSS Working Group WRB, 2007) – today surround the landfill and show an olive brown A-Bw-C profile. They are deep (the soil solum is around 95 cm), sub-alkaline, loamy and are characterized by a cambic horizon (Bw) showing a moderately strong subangular–blocky structure. Carbonates range from 41.9 to 75.3 g kg^{-1} , probably due to different deposition faces; organic carbon decrease regularly > with the depth (from 19.1 to 2.9 g kg^{-1}). Note the small amount of artefacts (around 3%) in the topsoil but only in the soils that surround the landfill. The main descriptive and analytical features related to the benchmark soil profile are reported in Tables 5 and 6.

As for the soils of the landfill (Fig. 5b), they were tailored in 1979 with wastes composed by fly ash of MSWI partially vitrified and glass ceramic (VFA) that, as previously reported, were suddenly covered with HTMs. During the soil survey of the landfill, from the top to the bottom (Fig. 2) we found: the HTM layer 20 cm depth; the VFA layer from 20 to 110 cm depth; the C1 horizon (subsoil layer: SS) from 90 to 125 cm depth; the C2 horizon (silty clay loam layer: SCL) from 105 to 235 cm depth; the 2C horizon (sandy loam layer: SL) from 230 to 100 cm depth. The main features of these man-made soils – Spolic Technosols (ecotoxic) according to the WRB (IUSS Working Group WRB, 2007) – are due to the presence of artefacts (backed earth; charcoal; glass–ceramic; vitrified fly) which are also responsible for the contrasting colours (reddish and greyish) and for the differences in clay, carbonates and organic carbon contents and for pH values (Tables 5 and 6).

As for the classification of these soils, the prefix Spolic indicates that they have a layer, 20 cm or more thick within 100 cm of the soil surface, with 20% or more (by volume, by weighted average) artefacts containing 35% or more (by volume) of industrial waste.

The suffix *Ecotoxic* indicates that these soils have within 50 cm of the soil surface sufficiently high and persistent concentrations of organic or inorganic substances to markedly affect soil ecology, in particular the populations of the mesofauna (IUSS Working Group WRB, 2007).

If we consider the features of the soil obtained after the VFA reclamation we should switch the soil classification at surface level from *Ecotoxic* to *Calcaric* because from the reclamation treatments we obtain a calcaric material (Fig. 5c) that fits the definition of the WRB for such material. The remediation with smectitic marlstone, as mentioned above, reduces the toxicity risks because of the carbonate precipitation.

4. Conclusions

Fly ash is generally classified as hazardous waste according to the European Waste Catalogue (European Union, 2002; SEPA, 2003) because of its high levels of soluble salts and particularly of heavy metals. The composition of municipal solid waste varies over time and from country to country, due to the differences in lifestyle and waste recycling processes; the ash content also varies. Generally, the chemical and physical characterization of ash depends on the compositions of the raw MSW, the operational conditions, the type of incinerator and air pollution control system design.

In our study case the use of a mixture of $\text{Ca}(\text{OH})_2$ and smectitic marlstone considerably reduced the leaching of trace elements such as Pb and Zn from the VFA material. This is due to the high coefficient of selectivity of the Ca-clay for elements with low ionic radius and low hydration energy.

Table 6
Main physical and chemical features of the pedons. The “caret” symbol (^) is used as a prefix to master horizon designations to indicate mineral or organic layers of human transported material.

| Pedon | Horizon (layers*) | Depth cm | Texture | | | pH H ₂ O | CaCO ₃ g kg ⁻¹ | Corg |
|-----------|-------------------|--------------|---------|----------------------------|------|------------------------|---|------|
| | | | Sand | Silt g kg ⁻¹ | Clay | | | |
| Fluvic | Ap | 0–50/60 | 222 | 533 | 245 | 7.9 | 52.4 | 19.1 |
| Cambisol | Bw | 50/60–70 | 274 | 525 | 201 | 8.1 | 41.9 | 9.4 |
| Siltic | BC | 70–95 | 173 | 602 | 225 | 8.2 | 75.3 | 7.1 |
| | C1 (SS) | 95–155 | 129 | 651 | 220 | 8.2 | 50.8 | 4.3 |
| | C2 (SCL) | 155–200+ | 620 | 303 | 77 | 8.3 | 49.9 | 2.9 |
| Spolic | ^A1 (HTM) | 0–20 | 190 | 488 | 322 | 7.8 | 94.6 | 9.9 |
| Technosol | ^A2 (VFA) | 20–40/130 | 756 | 175 | 69 | 6.3 | 03.5 | 20.6 |
| Ecotoxic | C1 (SS) | 40/130–165 | 137 | 632 | 231 | 8.1 | 54.5 | 3.8 |
| | C2 (SCL) | 165–270/400 | 187 | 602 | 211 | 8.2 | 51.6 | 2.1 |
| | 2C (SL) | 270/400–500+ | 587 | 322 | 91 | 8.6 | 50.5 | 1.3 |
| Spolic | ^A | 0–120/130 | 508 | 268 | 224 | 9.7 | 166.5 | 10.4 |
| Technosol | C1 (SS) | 40/130–165 | 143 | 629 | 228 | 8.0 | 49.7 | 2.9 |
| Calcaric | C2 (SCL) | 165–270/400 | 180 | 615 | 205 | 8.3 | 53.8 | 2.0 |

* Corresponding layers of the boreholes.

The Cu solubility of VFA is very high and VFA/CAM treatment did not interrupt the solubility and then the leaching. In fact, Cu has a lower affinity with the clay than the other metals.

It needs to be stressed that the reclamation of the VFA with Ca(OH)₂ and smectitic marlstone (VFA/CAM), stopped, in a relatively short period of time, any undesirable environmental impact deriving from the VFA presence.

The addition of marlstone with high carbonate content improves the overall quality of the environment we surveyed: the presence of carbonates drives the pedo-environment toward the development of an “eutric” character that allows for an easier development of the pedomesofauna and of the vegetation with its roots that, all in all thanks to the gradual release of CO₂ reduces the pH and promotes the precipitation of heavy metals in insoluble forms, such as carbonates or hydroxides.

The aspects linked to the soil reclamation have been clearly highlighted from the changes in the suffice of classification of the Technosols (from ecotoxic to calcaric) that can draw with immediacy the attention not only of specialists but also of stakeholders and politicians.

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References

- Alba, N., Gasso, S., Lacorte, T., Baldasano, J.M., 1997. Characterization of municipal solid waste incineration residues from facilities with different air pollution control systems. *J. Air Waste Manage. Assoc.* 47, 1170–1179.
- Albuquerque, C., Labrincha, J.A., 2008. Removal of contaminants from aqueous solutions by beds made of rejects of the lightweight aggregates production. *Ceram. Int.* 34, 1735–1740.
- Alloway, B.J., 1992. *Heavy metals in soil*. Blackie and Halsted Press, New York.
- Arpa, Ç., Say, R., Şatiroğlu, N., Bektaş, S., Yürüm, Y., Genç, Ö., 2000. Heavy metal removal from aquatic system by northern Anatolian Smectites. *Turk. J. Chem.* 24, 209–215.
- Bedelean, H., Măicăneanu, A., Burcă, S., Stanca, M., 2009. Removal of heavy metal ions from wastewaters using natural clays. *Clay Miner.* 44, 487–495.
- Bianchini, G., Natali, C., Di Giuseppe, D., Beccaluva, L., 2012. Heavy metals in soils and sedimentary deposits of the Padanian Plain (Ferrara, Northern Italy): Characterization and biomonitoring. *J. Soils Sediments* 12, 1145–1153.
- Bolt, G.H., Bruggenwert, M.G.M., 1976. *Soil chemistry — part A: Basic elements*. Elsevier, Amsterdam.
- Brookins, D.G., 1988. *Eh–pH diagrams for geochemistry*. Springer-Verlag, New York.
- Bryant, R.B., Galbraith, J.M., 2003. Incorporating anthropogenic processes in soil classification. In: Eswaran, H., Rice, T., Ahrens, R., Stewart, B.A. (Eds.), *Soil classification, a global desk reference*. CRC Press LLC, Boca Raton.

- Camps Arbertain, M., Madinabeitia, Z., Anza Hortalà, M., Macías-García, F., Virgel, S., Macías, F., 2008. Extractability and leachability of heavy metals in Technosols prepared from mixtures of unconsolidated wastes. *Waste Manag.* 28, 2653–2666.
- Cheeseman, C.R., Monteiro de Rocha, S., Sollars, C., Bethanis, S., Boccaccini, A.R., 2003. Ceramic processing of incinerator bottom ash. *Waste Manag.* 23, 907–916.
- Clark, R.N., Swayze, G.A., Wise, R., Livo, K.E., Hoefen, T.M., Kokaly, R.F., Sutley, S.J., 2003. USGS digital spectral library splib05a. USGS Open File Report 03-395.
- Clark, R.N., Swayze, G.A., Wise, R., Livo, K.E., Hoefen, T.M., Kokaly, R.F., Sutley, S.J., 2007. USGS digital spectral library splib06a. U.S. geological survey, digital data series 231.
- Dazzi, C., Monteleone, S., 2007. Anthropogenic processes in the evolution of a soil chronosequence on marly-limestone substrata in an Italian Mediterranean environment. *Geoderma* 141 (3–4), 201–209.
- Dazzi, C., Lo Papa, G., Palermo, V., 2009. Proposal for a new diagnostic horizon for WRB Anthrosols. *Geoderma* 151, 16–21.
- Decreto Legislativo n.152, 2006. Norme in materia ambientale. *Gazzetta Ufficiale* n. 88, 14 Aprile 2006-Supplemento ordinario n. 96.
- Decreto Ministeriale n.186, 2006. Individuazione dei rifiuti non sottoposti alle procedure semplificate di recupero, ai sensi degli articoli 31 e 33 del Decreto Legislativo del 1997, n. 22. *Gazzetta Ufficiale* n. 115 del 19/05/2006.
- Dudal, R., 2004. The sixth factor of soil formation. *Proceedings of International Conference on Soil Classification*. 3–5 August 2004. Petrozavodsk.
- European Union, 2002. European waste catalogue. http://www.nwcpo.ie/forms/EWC_code_book.pdf.
- European Union, 2006. Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the regions. Thematic strategy for soil protection plus summary of the impact assessment. COM 231 final pp. 1–12 (Brussels).
- Fanning, D.S., Balluff Fanning, M.C., 1989. *Soil: Morphology, genesis, and classification*. Wiley, New York.
- Franzini, M., Leoni, L., Saitta, M., 1975. Revisione di una metodologia analitica per fluorescenza-X basata sulla correzione completa degli effetti di matrice. *Rend. Soc. Ital. Mineral. Petrol.* 31, 365–378.
- García-Valles, M., Avila, G., Martínez, S., Terradas, R., Nogues, J.M., 2007. Heavy metal-rich wastes sequester in mineral phases through a glass–ceramic process. *Chemosphere* 68, 1946–1953.
- Hartley, W., Uffindell, L.A., Plumb, A.N., Rawlinson, H.A., Putwain, P., Dickinson, N.M., 2008. Assessing biological indicators for remediated anthropogenic urban soils. *Sci. Total Environ.* 405, 358–369.
- Haugsten, K.E., Gustavson, B., 2000. Environmental properties of vitrified fly ash from hazardous and municipal waste incineration. *Waste Manag.* 20, 167–176.
- Haynes, R.J., 2009. Reclamation and revegetation of fly ash disposal sites — Challenges and research needs. *J. Environ. Manag.* 90, 43–53.
- ICOMANTH, 2003. Circular letter n°4. <http://clic.cses.vt.edu/icomanth/circl4.pdf> (verified October 10, 2013).
- IUSS Working Group WRB, 2007. World reference base for soil resources 2006, first update 2007. World soil resources reports, 103. FAO, Rome.
- Jing, C., Meng, X., Korfiatis, G.P., 2004. Lead leachability in stabilized/solidifies soil samples evaluated with different leaching tests. *J. Hazard. Mater.* 114, 101–110.
- Johnson, C.A., Kersten, M., Ziegler, F., Moor, H.C., 1996. Leaching behaviour and solubility — Controlling solid phases of heavy metals in municipal solid waste incinerator ash. *Waste Manag.* 16, 129–134.
- Lam, C.H.K., Alvin, W.M., Barford, J.P., McKay, G., 2010. Use of incineration MSW ash: A review. *Sustainability* 2, 1943–1968.
- Lehmann, A., Stahr, K., 2007. Nature and significance of anthropogenic urban soils. *J. Soils Sediments* 7, 247–260.
- Leoni, L., Saitta, M., 1976. X-ray fluorescence analysis of 29 trace elements in rock and mineral standard. *Rend. Soc. Ital. Mineral. Petrol.* 32, 497–510.
- Li, Q., Wang, C., 2003. Cu nanostructure formed via redox reaction of Zn nanowire and Cu²⁺ containing solutions. *Chem. Phys. Lett.* 375, 525–531.

- Li, X., Bertos, M.F., Hills, C.D., Carey, P.J., Simon, S., 2007. Accelerated carbonation of municipal solid waste incineration fly ashes. *Waste Manag.* 27, 1200–1206.
- Lo Papa, G., Palermo, V., Dazzi, C., 2011. Is land-use change a cause of loss of pedodiversity? The case of the Mazzarrone study area, Sicily. *Geomorphology* 135 (3–4), 332–342.
- Monserie, M.F., Watteau, F., Villemain, G., Ouvrard, S., Morel, J.L., 2009. Technosol genesis: Identification of organo-mineral associations in a young Technosol derived from coking plant waste materials. *J. Soils Sediments* 9, 537–546.
- Morel, J.L., Schwartz, C., Florentin, L., de Kimpe, C., 2005. Urban Soils. In: Hillel, D. (Ed.), *Encyclopedia of soils in the environment*, 1–4. Elsevier, Oxford, UK, and St Louis, MO, USA, pp. 202–208.
- Park, Y.J., Heo, J., 2004. Corrosion behavior of glass and glass–ceramics made of a municipal solid waste incinerator fly ash. *Waste Manag.* 24, 825–830.
- Ribeiro, M.J., Albuquerque, C.M., Labrincha, J.A., 2008. Removal of lead and nickel ions in aqueous media by filtration through different clay-based beds. *Clay Miner.* 43, 647–656.
- Romero, M., Rawlings, R.D., Rincon, J.M., 1999. Development of a new glass–ceramic by means of controlled vitrification and crystallisation of inorganic wastes from urban incineration. *J. Eur. Ceram. Soc.* 19, 2049–2058.
- Sanchez, F., Barna, R., Garrabrants, A., Kosson, D.S., Moszkoviz, P., 2000. Environmental assessment of a cement-based solidified soil contaminated with lead. *Chem. Eng. Sci.* 55, 113–128.
- SEPA, 2003. Hazardous waste interpretation of the definition and classification of hazardous waste. Technical guidance WM2 Scottish Environment Protection Agency, Environment and Heritage Service, Environment Agency.
- Shim, Y.S., Rhee, S.W., Lee, W.K., 2005. Comparison of leaching characteristics of heavy metals from bottom and fly ashes in Korea and Japan. *Waste Manag.* 25, 473–480.
- Steiner, A.C., 2006. Foam glass production from vitrified municipal waste fly ashes. Eindhoven University Press, The Netherlands.
- SUITMA Wiki page, 2013. http://ticri.inpl-nancy.fr/urban_soils.en/index.php/Main_Page (verified October 10, 2013).
- Takeo, N., 2005. Atlas of Eh–pH diagrams. Intercomparison of thermodynamics databases. Geological survey of Japan open file report no. 419.
- Traina, S.J., Doner, H.E., 1985. Co, Cu, Ni and Ca sorption by a mixed suspension of smectite and hydrous manganese dioxide. *Clay Clay Miner.* 33 (2), 118–122.
- Vittori Antisari, L., Trivisano, C., Gessa, C., Gherardi, M., Simoni, A., Vianello, G., Zamboni, N., 2010. Quality of municipal wastewater compared to surface waters of the Rivers and artificial canal network in different areas of the Eastern Po Valley (Italy). *Water Qual. Expo. Health* 2, 1–13.
- Vittori, Antisari L., Carbone, S., Ferronato, C., Simoni, A., Vianello, G., 2011. Characterization of heavy metals atmospheric deposition for assessment of urban environmental quality in the Bologna city (Italy). *EQA* 7, 49–63.
- Wójtowicz, A., Stórkłosa, A., 2002. Removal of heavy metal ions on smectite ion-exchange column. *Pol. J. Environ. Stud.* 11 (1), 97–101.
- Yang, J., Xiao, B., Boccaccini, A.R., 2009. Preparation of low melting temperature glass–ceramics from municipal waste incineration fly ash. *Fuel* 88, 1275–1280.
- Yao, F.X., Macías, F., Virgel, S., Blanco, F., Jiang, X., Camps Arbestain, M., 2009. Chemical changes in heavy metals in the leachates from Technosols. *Chemosphere* 77, 29–35.
- Zipser, C., Komarneni, S., Baker, D.E., 1988. Specific cadmium sorption in relation to the crystal chemistry of clay minerals. *Soil Sci. Soc. Am. J.* 52, 49–53.