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Assessment of Mechanical Resistance, γ-radiation Shielding and Leachate γ-radiation of Stabilised/solidified Radionuclides Polluted Soils: Preliminary Results

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Stabilisation/solidification treatment was performed in order to assess the possibility to remedy radionuclides (^{232}Th) polluted soils. A sandy soil spiked by thorium oxide (ThO_2) at level of 2.2 % was stabilised/solidified using different binder mixture of Portland cement (32.5 Rck and 42.5 Rck) and barite aggregates at different soil:binder ratio (3.3:1 and 4.0:1) and tested for its setting time, unconfined compressive strength (UCS), γ radiation shielding and contaminant leaching.
Results obtained by setting time tests showed that different treatments do not influence the performance of the treatment, whereas the level and the type of cement used significantly influenced the mechanical resistance of the S/S materials. The presence of the barite aggregates mixed with cement gives also a significant containment of the γ radiation and an excellent reduction of contaminant leaching but slightly reduce the performance in terms of mechanical resistance, possibly representing an optimal choice to S/S treat low level radionuclides polluted soil. The obtained preliminary results are of scientific and practical interest and may be used for further researches, whereas complete results will represent a suitable tool to optimize the treatment operating conditions and to guide the design and the scale-up of S/S treatment systems of full scale remediation activities of radionuclides polluted soils.

1. Introduction

Soil contamination caused by artificial radionuclides is a serious problem worldwide. Radionuclides are introduced in the environment following nuclear power plant accident or nuclear, military and scientific activity (Guidi et al., 2009). Radionuclides can travel around the world on air streams, and due to their weight, settle to the soil surface. In addition, they can be dissolved in solution and then move into the water resulting in a downward metal migration and thus in a groundwater pollution (Gavrilescu et al., 2009). Among radionuclides, ^{232}Thorium (^{232}Th) with ThO_2 is widely used in the world and represents a permanent source of soil and water pollution due to its increased solubility in water at high pH values (Wierczinki et al., 1998).
The remediation of radionuclides polluted soils or their immobility in uppermost soil layers represent a key factor for environment and human health. Limited investigations have been performed to assess the remediation of radionuclides polluted soil by selected treatments. Physical treatments including soil-washing or electrokinetic decontamination processes have been successfully proposed by AbdEl-

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Sabour (2007) and Kyeong-Hee et al. (2003), respectively. Chemical extraction was showed to be adequate for the remediation of uranium polluted soils (Francis and Dodge, 1998), whereas for long-time project and upper soil layer contamination, phytoextraction could be considered a suitable solution (Hashimoto et al., 2005). However, the above-mentioned treatments may be too expensive due to their excavation and transport or energy costs, or long time required as in the case of phytoextraction technique. Furthermore a last tendency is to remedy polluted soils using in situ technology in order to save costs and avoid a further pollution during the transport.

Stabilisation/solidification (S/S) has been widely used due to its versatility, efficiency, time and costs to dispose of low-level radioactive and hazardous wastes (Sun et al., 2011), as well as to in situ remedy metal contaminated soils (Lin et al., 1996). Stabilization is a process where additives are mixed with waste or soil to determine a high alkaline mixture in order to fully or partially bound the contaminants and thus minimize the rate of their migration. Likewise solidification is a process employing additives such as binder by which the physical nature of the soil (strength, compressibility, permeability and durability) is altered after the treatment (Lin et al., 1996). Most S/S applications are Portland cement (PC)-based, but PC can be combined with other minerals such as blast-furnace slag, lime and/or fly ash and or adsorbent materials (clays) (Meneguin et al., 2011). In metal polluted soils treated with PC, three possible mechanisms may be responsible for the immobilization of contaminants during the hydration phases: precipitation resulting from the formation of metal silicate oxide, inclusion, either by physical encapsulation and or chemical inclusion and metal incorporation by the sorption on fine materials.

Therefore, S/S can represent an optimal choice for radionuclides polluted soils treatment also due to the possibility to use specific materials such as Portland cement and barite aggregate, for which the shielding properties in conventional radiation attenuation process (i.e.: nuclear central buildings) are known (Kharita et al., 2010; Shaaban and Assi, 2011), in order to achieve an in situ contaminant radiation shielding. However, the possibility to treat radionuclides polluted soil by PC based S/S has never been investigated.

The objective of this research was to investigate the potential of S/S technique for radionuclides polluted soils treatment and, specifically, the influence of binder mixtures (PC and barite aggregate) on mechanical and setting features, radiation shielding and contaminant leaching of stabilised/solidified ^{232}Th polluted soil. Preliminary results are proposed in this work. Complete results will represent a suitable tool to optimize the treatment operating conditions and to guide the design and the scale-up of S/S treatment systems for the remediation of radionuclides polluted soils.

2. Experimental

2.1 Soil, contaminants and binder systems

A sandy soil with properties shown in Table 1 was spiked by Thorium oxide (ThO_2) at level of 2.2 % and different S/S treatments were performed by mixing spiked soil (S) with two types of Portland cement (PC) (32.5 Rck and 42.5 Rck) or with PC (42.5 R_{ck}) and barite aggregates (B) at two S:C ratio (4:1 and 3:1). Conventional water (W) to cement (C) ratio of 0.42:1 was adopted for all mixtures.

Table 1: Characteristics of the sandy soil selected for the experiments

Parameter	Value
Sand (silica sand 75-350 μm) (%)	80.0
Silt (silica flour 10-75 μm) (%)	10.0
Clay (kaolin <75 μm) (%)	10.0
pH (L:S of 10)	8.73
Organic matter (%)	2.79
Bulk density (g cm^{-3})	1.42
Surface area (m^2 g^{-1})	3.33
Moisture content (%)	14.0

The experimental matrix is given in Table 2.

Table 2: Experimental matrix

Label	S:C ratio	Cement type (R_{ck})	W:C ratio	Barite
A1	4:1	32.5	0.42:1	No
A2	4:1	42.5	0.42:1	No
A3	3:1	32.5	0.42:1	No
A4	3:1	42.5	0.42:1	No
B1	3:1	42.5	0.42:1	Yes

2.2 Production of S/S samples and testing protocol

Mixing was performed by means of a food mixer for 15 min to a homogeneous consistence. Treated soil samples were cast and compacted into cylindrical moulds (100.0 mm in height and 50.0 mm in diameter) in accordance with the ASTM D1557-91 (1993) standard or directly used for setting time test. After 1 day, samples were demoulded then cured for 28 days in sealed sample bags at a temperature of 20 ± 2 °C and a relative humidity of 95 ± 3 % prior to testing.

To verify the effectiveness of the S/S treatment, it is necessary to assess the characteristics of the treatment products and compare them with specific performance criteria.

Testing protocol on S/S treated soils included the following tests: setting time, unconfined compressive strength (UCS) and leaching. UCS test relate the mechanical resistance of the S/S products and it was performed according to ASTM test method D1633 (1993). The setting time of a cementitious mixture is referred to as the period from which water is introduced into the mixture system to the onset of hardening. The initial setting time occurred when the Vicat needle 1.00 mm in diameter penetrated the mortar mixture to a point 25 ± 1 mm, while final setting time occurred when the needle did not sink visibly into the paste (ASTM C191-82, 2004). In order to assess the leaching behaviour of the contaminant before and after the treatment, the monolithic (A1 and B1 treatments) and the contaminated soil samples were leached following the abbreviated ANSI/ANS-16.1 (1986) procedure for an immersion time of 32 h.

Gamma Radiation Shielding (γRS) of S/S monolithic samples was chosen as representative parameter to assess the effectiveness of the treatment in terms of limitation of the radioactivity effects by means the selected treatment. γRS was calculated using the following expression.

$$\gamma RS = (CPS_{Soil} - CPS_{S/S\ Soil}) \cdot 100 / CPS_{Soil}\ (\%) \qquad (1)$$

where CPS_{Soil} is the γ-ray counting rate measured for the contaminated soil sample and $CPS_{S/S\ Soil}$ is the γ-ray counting rate measured for the same sample after the S/S treatment.

Both counting rates are due to the presence of ^{232}Th decay products, as well as to the natural background of all the used materials.

For the evaluation of the treatment efficiency in terms of leaching, the Gamma Radiation Reduction (γRR) in leachate was calculated using the following expression:

$$\gamma RR = [(CPS_{L,\ Soil} - CPS_{water}) - (CPS_{L,\ S/S\ Soil} - CPS_{water})] \cdot 100 / (CPS_{L,\ Soil} - CPS_{water})\ (\%) \qquad (2)$$

where $CPS_{L,\ Soil}$ is the γ-ray counting rate measured for the leachate from contaminated soil sample, $CPS_{L,\ S/S\ Soil}$ is the γ-ray counting rate measured for the leachate from the S/S contaminated soil sample and CPS_{water} is the γ-ray counting rate measured for bi-distillate water used for the leaching test.

2.3 γ-ray emission measurement

The γ-ray counting rate was measured using a low level γ-ray counting spectrometer including a 2” x 2” NaI(Tl) detector for the solid samples measurements (horizontal and vertical position) (Figure 1-a), and a 2” x 2” HPGe for the leachate sample and water measurements (Figure 1-b). In both cases the detector was surrounded by a 10 cm thick lead shield to smooth the background γ-radiation, and it was connected to a multichannel pulse height analyzer and to laptop for parameters acquisition and analysis. For each solid sample position the measurement was carried out for a total period of 1000 s, whereas for the liquid samples the period was 86,400 s. For the liquid sample measurements only the contribution of 238.6 (43.6 %), 338.3 (11.4 %), 583.2 (85 %), 860.6 (12.5 %), 911.2 (26.2 %) and 969.0 (15.9 %) keV γ-ray energies was considered (Degering and Kohler, 2011).

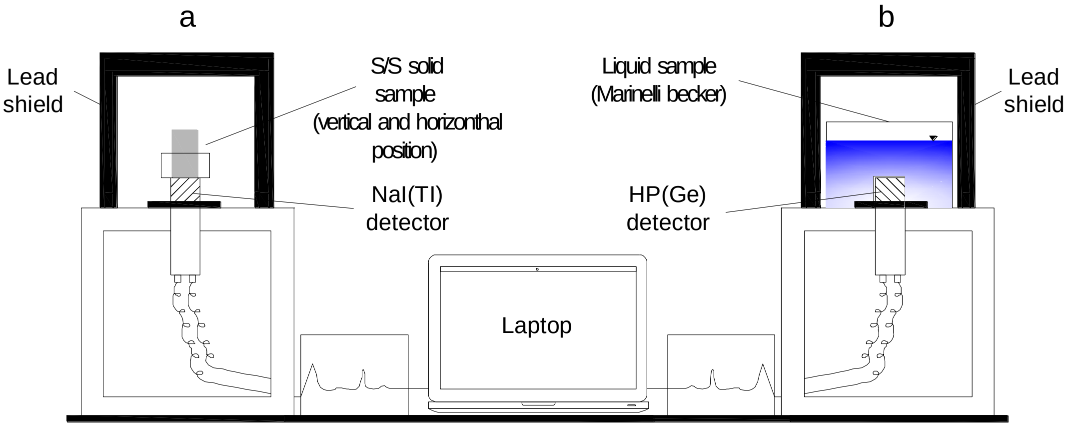

Figure 1: Schematic of the spectrometer used for counting of γ-ray emitted by solid (a) or liquid (b) samples.

3. Results and discussion

Results obtained by setting time tests (Table 3) showed that different treatments did not influence the setting time value and adequate final setting time (<72 h) for all the investigated treatments.

Table 3: Setting time values for all the investigated S/S treatment

Label	Initial setting time (h)	Final setting time (h)
A1	1.2	3.0
A2	1.2	3.0
A3	1.4	3.2
A4	1.4	3.2
B1	1.3	3.0

Results of compressive strength (UCS) tested at 28 days of curing and γRS for all the investigated treatments are presented in Figure 2-a and Figure 2-b respectively. Results showed that the level and the type of cement used significantly influenced the performance of the treatments in terms of compressive strength. Specifically, as expected, an increase of UCS was observed with increasing the percentage of binder and with using the 42.5 Rck type PC.. In terms of quality acceptance, considering the US EPA criteria (minimal UCS value = 3.5 MPa) for the non hazardous waste landfill disposal, insufficient strength value was observed only for A1 treatment. In the case of hazardous waste landfill disposal, for which a minimal UCS value of 0.35 MPa is required, all the investigated treatments are adequate. Setting time and UCS results are in agreement with other literature findings where experimental values in the same range were observed (El-Kamash et al., 2006; Lin et al., 1996).

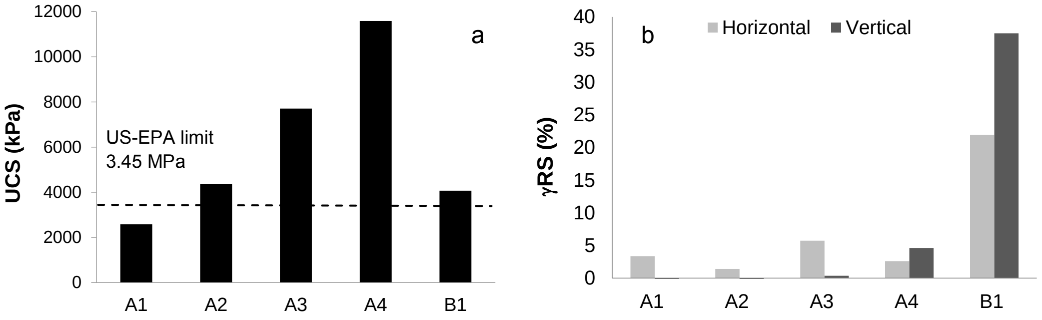

Figure 2: UCS (a) and γRS(%) (b) values for all the investigated S/S treatment

Limited γRS values (up to about 5 %) were observed for all treatments except than for B1 (vertical position) for which a shielding higher than 35 % was observed. The good effectiveness of the shielding treatment for B1 is clear by comparing γ-ray energy spectra. The same gamma ray contribution was measured before and after the A2 treatment (Figure 3-a), while the counting rate was significantly reduced after the B1 treatment (Figure 3-b). Moreover, γRR values of (83 ± 4) % and (102 ± 4) % were measured for the treatments A1 and B1 respectively (Table 4).

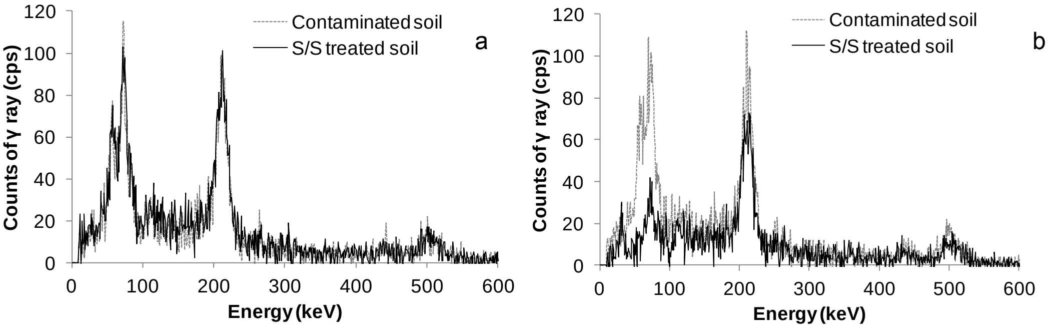

Figure 3: γ-ray energy spectrum for contaminated and S/S treated soil samples for A2 (a) and B1 (b) treatments

Table 4: Counts of γ-ray and γRR (%) for A1 and B1 treatments

Label	$CPS_{L,\ Soil}$	$CPS_{L,\ S/S\ Soil}$	CPS_{water}	γRR (%)
A1	4490	2356	1917	83 ± 4
B1	4490	1863	1917	102 ± 4

This aspect is relevant because highlights the possibility, for a S/S with cement and barite, to combine chemical and physical processes, aimed to give specific mechanical features to treated soils, with the possibility to obtain a containment of the soil γ-radiation and a γ-radiation reduction of the leachate.

4. Conclusion

The following conclusions have been drawn according to the results presented above:

- Results obtained by setting time and UCS tests showed that different treatments did not influence the setting time value and adequate final setting time for all the investigated treatments, whereas the level and the type of cement used significantly influenced the performance of the treatments in terms of compressive strength.

- The presence of the barite aggregates mixed with Portland cement gives a significant containment of the radioactivity effects and contaminant leaching but reduce the mechanical resistance.
- The binder mix B1 could represent the best choice to remediate a low level radionuclides polluted soil by means of a S/S treatment with the possibility to obtain an in situ containment of the radioactivity effects and a contaminant reduction and thus radioactivity level in leachate.
- The obtained results are of scientific and practical interest and may be used for further researches, whereas complete results will represent a suitable tool to optimize the operating conditions and to guide the design and the scale-up of S/S remediation of radionuclides polluted soils.

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