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Stabilisation/solidification of Radionuclides Polluted Soils: a Novel Analytical Approach for the Assessment of the γ-radiation Shielding Capacity

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Soil contamination caused by γ-radiation emitter radionuclides is a serious problem worldwide. Cement-based Stabilisation/solidification (S/S) could represent an optimal choice to treat radionuclides polluted soils due to the possibility to shield the γ-radiation emitted by contaminant.
In order to better planning the treatment procedures, a novel analytical approach has been developed and applied in order to assess the γ-radiation shielding (γRS) of cylindrical S/S treated bodies taking into account the shielding properties of materials used in S/S treatment, all the parameters related to nuclear processes involved and the interaction between radiation and matter. Calculations were compared with γRS values obtained by *bench-scale* experimental activities. For experiments a soil spiked by thorium oxide (ThO_2) was stabilised/solidified using different binder mixture of Portland cement and barite aggregates at different soil:binder ratios and tested for its γ-radiation shielding properties.
Results obtained showed that the presence of the barite aggregates mixed with cement gives a significant containment of the γ-radiation possibly representing an optimal choice to S/S treat low level radionuclides polluted soil. Furthermore, a good correspondence between analytical and experimental data was observed making the proposed analytical approach a potential suitable tool to great simplify the estimation of γ-radiation shielding properties of several binders-materials-radionuclides S/S systems.

1. Introduction

Radionuclides polluted soil is a serious problem worldwide and it currently represents a living matter (Guidi et al., 2009). In the last year, also supported by the tragic events of Fukushima (Japan) disaster, a huge effort has been made by several scientists to study this issue (Antovic et al., 2012; Evseeva et al., 2012).
Radionuclides are introduced in the environment following nuclear power plant accident or nuclear, military and scientific activity, resulting in both soils and groundwater pollution (Hu et al., 2010). Due to the long half-lives of many of these radionuclides, the presence of radioactively contaminated soils, especially around nuclear sites, presents a long-term environmental concern and may constrain the extent to which sites can be redeveloped and re-used following decommissioning.
Among radionuclides, isotopes able to generate gamma (γ)-radiation have high radiotoxicity and they are of major concern in the environment (Falciglia et al., 2012). In physics, gamma radiation, also known as γ-rays, is an electromagnetic radiation of high frequency and energy produced by the decay from high energy states of atomic nuclei (gamma decay), after they have emitted either alpha (α) or beta (β) particles. Both α and β particles have an electric charge and mass, and thus are quite likely to interact with other atoms in their path. Instead, γ-radiation is composed of photons, which have neither mass nor electric charge, penetrates much further through matter than either α or β radiation, being thus biologically

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hazardous. Radionuclides radiotoxicity is due to their decay processes, which, by means energy emissions as α, β and γ rays, can ionize biological tissues and therefore damage them.
Limited chemical-physical (Agnew et al., 2011; Kim et al., 2011) or biological (Duquène et al., 2009; Mihalik et al., 2012) environmental restoration methods for radioactively contaminated soils have been developed and studied and thermal treatments can be successfully applied only for organic pollutants removal (Falciglia et al., 2011). Furthermore, all these treatments may be prohibitively costly, time consuming or environmentally unsustainable such as disposal in landfills if large areas of land are involved.
Cement-based Stabilisation/soilidification (S/S) technique was successfully proposed to treat radionuclides polluted soils (Falciglia et al., 2012).
S/S is an in situ remediation technique by which Portland cement (PC) or other binders are mixed with contaminated soils in order to produce high resistance solidified columns of a high alkaline mixture where contaminants are bounded. PC can be combined with other materials such as ground granulated blast-furnace slag (GGBS), fly ash from coal-fired power generation (pulverised fuel ash (PFA)), cement kiln dust (CKD), and clays in order to give specific properties or reduce the amount of cement.
The choice of the materials employed in S/S represents a key factor of the treatment due to the material γ-radiation absorption, or mechanical and immobilisation properties. However, very few information are available on the γ-radiation shielding properties of selected S/S treatments, due to the hazards and the high costs of *lab-scale* experiments on radionuclides pollution, making unclear the application of S/S in real contamination cases. Therefore, a valuable tool for assessing the influence of the S/S treatment on the in situ γ-radiation shielding properties could be essential.
In this work, a novel analytical approach has been developed and applied taking into account the shielding properties of materials used in S/S treatment, all the parameters related to nuclear processes involved and the interaction between radiation and matter. Calculations were compared with experimental results obtained by *bench-scale* experiments. The analytical approach described could represent a suitable tool with the potential to great simplify the estimation of γ-radiation shielding properties of in situ S/S treatments.

2. Experimental

2.1 Soil contamination and binder systems

Among radionuclides, Thorium (Th) is an actinide element which has a very stable tetravalent oxidation state. ^{232}Th naturally decays through a 10-step chain to ^{208}Pb, a stable isotope. α and β particles as well as γ-rays are emitted during this decay. According to Environmental Protection Agency (EPA) the primary sources of Th at the Superfund sites are processing and extraction of Th, U and Ra from ores or ore concentrates. Disposal of incandescent lights and lanterns containing ^{232}Th are an additional source of Th contamination (Bhatti et al., 2012). ^{232}Th as soil pollutants presents both a toxic and radiological hazard and it can be used as an analogue for other radionuclides. In fact, Thorium oxide has a low radiotoxicity and can be used to simulate high radiotoxicity contamination such as Pu (Larson et al., 2005). ^{232}Th also presents sorption properties and interaction mechanism with cement hydration products similar other radionuclides such as P and U (Evans, 2008).
For the above reason, ^{232}Th as thorium oxide (ThO_2) was selected as radionuclide contaminant for the experiment and used for spiking a sandy soil at level of 2.2 %. Different S/S treatments were performed by mixing 190 g of 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. The experimental matrix is given in Table 1.

Table 1: Experimental matrix

Treatment	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 γRS measurement

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. After 1 d, samples were demoulded then cured for 28 d in sealed sample bags at a temperature of 20 ± 2 °C and a relative humidity of 95 ± 3 % prior to measurement activities.
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.

$$\gamma RS = \frac{(CPS)_{soil} - (CPS)_{S/S\ soil}}{(CPS)_{soil}} \cdot 100\ (\%) \quad (1)$$

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.
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 position) (Figure 1). 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 the measurement was carried out for a total period of 1,000 s.

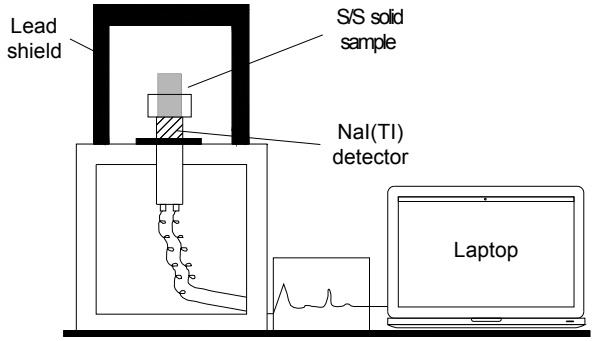

Figure 1: Schematic of the spectrometer used for counting of γ-ray emitted by polluted soils and S/S treated samples

3. Attenuation of γ-rays in materials and analytical approach

It is well know that the attenuation of γ-rays in a given material is a function of γ-ray energy, the elemental composition, the density and the thickness of the material. The attenuation is a nonlinear function of the thickness (x) of the material, described by the Lambert-Beer law (Knoll, 2000):

$$I(x) = I_0 e^{-\mu x} \quad (2)$$

where I(x) is the transmitted intensity, I_0 is the incident intensity and μ (cm^{-1}) is the linear attenuation coefficient of the material. μ is often expressed as a function of the mass attenuation coefficient, μ_m ($cm^2\ g^{-1}$):

$$\mu = \mu_m \rho \quad (3)$$

where ρ (g cm^{-3}) is the density of the material. For a mixture of *n* number of different materials it is necessary to calculate μ as weighted average of the single μ values of the different materials.
For the case of a cylindrical body, on this basis it comprises an infinite number of tubes of negligible thickness and assuming that the γ-rays are radiated only radially by the body, the total number of γ-rays emitted by the body as a function of cylinder's radius (r) at a fixed energy (KeV) can be calculated by the following equation (Gamage and Joyce, 2011):

$$I(r) = \frac{2\pi\rho\gamma h}{\mu^2}\left[r\mu - 1 + e^{-\mu r}\right] \quad (4)$$

Where γ is the number of the counts per second (CPS) per gram of γ emitter radionuclides (contaminant) at a fixed emission energy.

Based on equations (1) and (4), the γ radiation shielding (γRS) of a S/S treated soil cylindrical samples can be calculated for any given S/S treatment at fixed decay energy by the expression:

$$\gamma RS_{c[E]} = \frac{\left(\frac{\left[r\mu-1+e^{-\mu r}\right]}{\mu^2}\right)_{soil} - \left(\frac{\left[r\mu-1+e^{-\mu r}\right]}{\mu^2}\right)_{S/S\ soil}}{\left(\frac{\left[r\mu-1+e^{-\mu r}\right]}{\mu^2}\right)_{soil}} \cdot 100\ (\%) \qquad (5)$$

where r is the radius of the cylindrical soil sample and μ is the linear attenuation coefficient for untreated soil (soil) or S/S treated soil (S/S soil) at a fixed decay energy (E).

In this work γRS_c values were assessed using eq. (5) for the treatments A1, A2, A3, A4 and B1, and results were compared to γRS_m values obtained by measurements using the low level γ-ray counting spectrometer. $\gamma RS_{c[E]}$ was calculated for three different energies: 57.96, 69.72 and 210.84 KeV. For any selected energy and treatment, μ was obtained by equation (3) and μ_m was calculated by means XCOM software (Gamage and Joyce, 2011) considering the percentage composition of binder mixture of each treatment and the nuclear effects of interaction between radiation and matter: photoelectric and Compton scattering.

γRS_c was obtained as average of the three $\gamma RS_{c[E]}$ values. Finally, for the validation of the analytical method, an analytical correction factor (CAF) was applied to assess the consistence of analytical data with experimental results.

4. Results and discussion

The variation of total mass attenuation coefficient (μ_m) as a function of the incident γ-ray energy (photon energy, E) calculated by XCOM for untreated contaminated soil and S/S treatments A1, A2, and B1, is reported in Figure 2. For all the samples, μ_m decreases with photon energy (E) decreasing, denoting a reduction of the γ-ray absorbing properties of the tested materials with increasing of decay energy values. Highest μ_m *values* were found for B1 treatment due to the presence of barite aggregate as a partial replacement for Portland cement, due to the ability of barite to increase the shielding properties of the binder mixture. μ_m values observed were reflected to γRS_c values calculated by equation 4 (Table 2). Limited γRS_c values (up to about 5 %) were observed for all treatments except than for B1 for which a shielding higher than 30 % was observed.

The validity of the analytical method proposed in this research has been explored by comparing calculated data with experimental findings. The results obtained from the calculation were plotted along with those from the experimental measurements by way of comparison in Figure 3. Such a preliminary set of data exhibit an excellent (R^2=0.992) linear correspondence between the calculated and the experimental results. A wider data set measurements is needed in order to have a more detailed correspondence between analytical and experimental data. The linear dependence observed allows the application of an analytical correction factor, CAF, expressed as:

$$CAF = \frac{\gamma RS(experimental)}{\gamma RS(analytical)} \qquad (6)$$

CAF was calculated and the results for each treatment was reported in Table 2. CAF values in the range 0.71-1.22 are consistent with findings reported by other authors (Gamage and Joyce, 2011) and highlight a good correspondence between analytical and experimental data, making the proposed analytical approach a potential suitable tool to great simplify the estimation of γ-radiation shielding properties of binders and materials employed in situ S/S treatment.

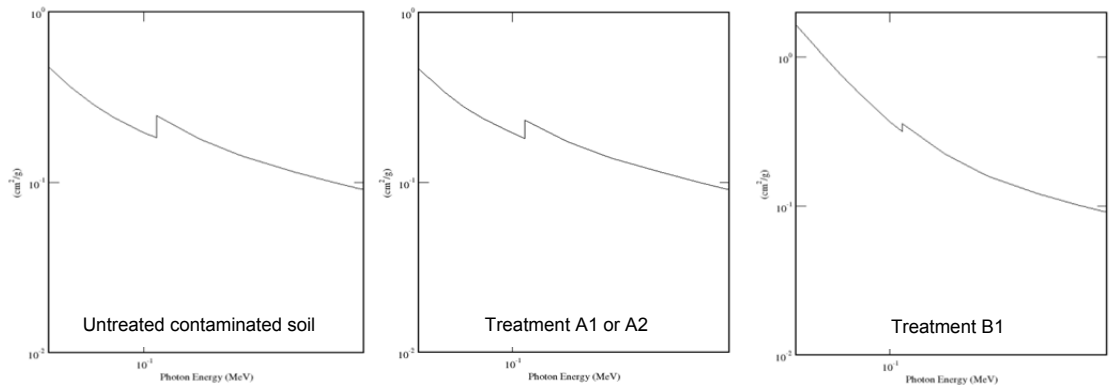

Figure 2: The variation of total mass attenuation coefficient (μm) with the incident γ-ray energy (photon energy, E) for untreated soil and S/S treatments A1, A2, and B1

Table 2: Comparison of results from analytical method with experimental data for untreated soil and S/S treatments A1, A2, A3, A4 and B1

Treatment	*Energy (keV)*	*ρ (kg cm^{-3})*	*μ (E) (cm^{-1})*	*$\gamma RS_{c[E]}$ (%)*	*γRS_c (%)*	*γRS_M (%)*	*CAF*
Untreated soil (soil)	*57.96*	1.39	0.52				
	69.72		0.40				
	210.84		0.20				
A1	*57.96*	*1.40*	0.51	3.36	2.50	2.53	1.01
	69.72		0.39	2.75			
	210.84		0.19	1.40			
A2	*57.96*	*1.40*	0.51	3.36	2.50	1.86	0.72
	69.72		0.39	2.75			
	210.84		0.19	1.40			
A3	*57.96*	*1.49*	0.54	5.52	4.12	5.05	1.22
	69.72		0.42	4.50			
	210.84		0.21	2.33			
A4	*57.96*	*1.49*	0.54	5.52	4.12	3.02	0.73
	69.72		0.42	4.50			
	210.84		0.21	2.33			
B1	*57.96*	1.65	*1.91*	50.36	33.9	24.2	0.71
	69.72		*1.31*	39.10			
	210.84		*0.26*	34.49			

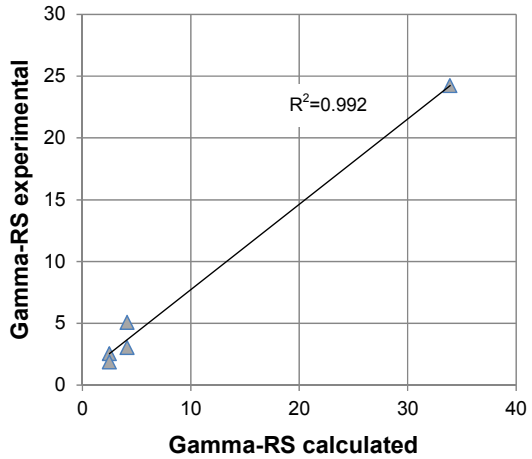

Figure 3: Gamma-RS: analytical VS experimental (treatments A1, A2, A3, A4 and B1)

5. Conclusions

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

- The presence of the barite aggregates mixed with Portland cement gives a significant containment of the radioactivity effects making the binder mix B1 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.
- The analytical approach proposed could represent a suitable tool to great simplify the estimation of γ-radiation shielding properties of binders and materials employed in situ S/S treatment, allowing the estimation of γ-radiation emitted by any type of S/S treated soil polluted considering any selected high radiotoxicity radionuclides at any contamination level.
- 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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