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Investigation on Novel High–Density Grouts for In Situ Stabilisation/Solidification of ^{137}Cs–Contaminated Soils

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Gamma-ray shielding and Cs immobilisation of high-density magnetite (MG) and iron powder (IP) in Portland cement (PC) based-S/S treatment of Cs – contaminated soils were investigated. Gamma ray spectrometer with High Purity Germanium (HPGe) detector was used for γ-ray emission measurement. Main results reveal that the replacement of PC by MG or IP (up to 50%) leads to a marked increase (up to about 4-fold) in the γ-ray shielding performance. A higher MG amount leads to a decrease that performance. The highest γRS index of ~26% (662 keV) was found in the case of IP addition (33.3%). The use of MG-mixtures allows reaching slightly slower γRS index jointly with the highest Cs-immobilisation of 97.8%. Results revealed MG - PC S/S as the best choice and could provide a basis for decision-making of S/S remediation of ^{137}Cs-contaminated sites.

1. Introduction

Artificial radionuclides released in the environment due to nuclear weapon tests, nuclear energy or scientific activity represent a great concern worldwide (Falciglia et al., 2012). Released high volatility fission products presents both a chemical and a radiological hazard (Olise et al., 2013) and this poses a major concern for environment and human health (Falciglia et al., 2013). Furthermore, radionuclide soluble forms can be dissolved in water, resulting in a potential groundwater pollution. In particular, soils contaminated with long-life gamma (γ)-emitter radionuclides have a long-term radiological impact (Fuma et al., 2015). γ-radiation has neither mass nor electric charge, and can penetrate, ionize and damage biological tissues, representing a long - term hazard to human health. Among γ - emitting radionuclides, cesium-137 (^{137}Cs) is the major source of soil contamination worldwide representing a severe health risk due to its high biological availability and long - term radiologic impact (30 years half-life) (Malins et al., 2016). Landfill disposal of ^{137}Cs - contaminated soils is an unsafe solution and this makes remediation strategies strictly required (Mallampati et al., 2015). Very limited techniques have been proposed, including biological or chemical - physical treatments (Wang et al., 2012; Kim et al., 2010). However, these solutions generally have several limitations, among which needing for landfill disposal of the produced high - radioactive wastes. Furthermore, in situ management of contaminated sites is preferable (Groudev et al., 2010).

In-situ Portland cement (PC) - based S/S has been recognised as an efficient, low-risk and cost-effective treatment with a high versatility that does not produce contaminated by-products needing landfill disposal (Falciglia and Vagliasindi, 2013; Falciglia et al., 2014a; Wang et al., 2015). In addition, the replacement of PC by other products or recycled wastes is widely accepted due to the reduced environmental impact and improved material properties such as lower permeability (Jin et al., 2016) or higher radiometric shielding. Recent investigations (Falciglia et al., 2014b; 2015) demonstrated that the replacement of PC by barite powder (BA) resulted in an improvement of the S/S performance both in terms of γ-radiation emission and contaminant leaching reduction. However, experimental results showed the necessity of investigating new promising S/S shielding mixtures. Due to their high density, as well as their relative inexpensiveness and ready availability (Ouda, 2015), magnetite (MG) and iron powder (IP) could be perfect candidates to produce MG- or IP-bearing grouts with improved γ-radiation shielding properties. In addition, MG has been reported to

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have high immobilisation capacities for a wide range of contaminants (Karami, 2013; Kumari et al., 2015). On the other hand, the presence of a complex geometry such as in the case of S/S system makes the problem of assessing the γ-ray incident intensity transmitted after the S/S treatment more difficult to be solved and γRS index an indispensable tool (Falciglia et al., 2015).

The main aim of the present work was to assess the γ-ray shielding as γRS index and leaching reduction performance of novel MG - and IP - cement mixes in S/S treatments of Cs - contaminated soils.

2. Materials and methods

2.1 Artificial contamination procedures and grout systems

Soil contamination was simulated by mixing a reagent grade ^{133}Cs soluble salts (CsCl) solution (Mallampati et al., 2015) with a model sandy (80% sand 75-350 μm; 10%silt; 10% clay) soil free of contamination. Then, contaminated soil samples (Cs content = 5.0 wt%) were stored for 1 month before analysing for Cs concentration (ICP-OES) and simulated S/S treatments. For soil samples aimed at γRS index calculation, γ-radiation emission was simulated using thorium 232 (^{232}Th in the form of ThO_2) (Falciglia et al., 2015).

For the experiments, PC (CEM I) was selected as binder, with MG (Fe_3O_4) and IP as high-density shielding materials (SM) (Table 1). S/S was simulated by mixing contaminated soil samples with PC - MG or PC - IP grout mixes at different PC : SM ratios with a soil : grout (S : G) proportion of 3 : 1. PC : MG and PC : IP ratio of 1 : 1 was selected for investigating the influence of different S : G ratios.

Table 1: Characteristics of the Portland cement (PC) and shielding materials (BA, MG and IP)

	Portland cement (PC)	*Magnetite (MG)*	*Iron powder (IP)*	*Barite (BA)*
Chemical composition (%)	SiO_2 (23.5) Fe_2O_3 (3.7) Al_2O_3 (4.9) CaO (66.3) MgO (1.6)	Fe_3O_4 (>95)	Fe (>98)	$BaSO_4$ (> 95)
Properties				
Texture (μm)		10-105	10-105	10-105
Bulk density (g cm^{-3})	1.21	3.60	3.83	3.32
Surface area (m^2 g^{-1})	0.78	16.98	0.11	10.05

For a better comparison of the results, novel additional data from Falciglia et al. (2015) were obtained. S/S soil samples were prepared in accordance with the ASTM D1557-91 (1993) standard and cured for 28 days before γ - ray emission measurement or leaching test. After the curing process, the density (ρ) and the total porosity (ф) of each produced mix were also assessed (Falciglia et al., 2015).

2.2 γRS index assessment and leaching procedures

For each mixture, γRS index was calculated using Eq. 1, considering the emission energy range 74.81 - 968.94 keV (Falciglia et al., 2017):

$$\gamma RS=\frac{I_{Soil}-I_{SS}}{I_{Soil}}\cdot 100\ (\%) \qquad (1)$$

γ-ray counting rate (CPS) emitted from samples was measured before (I_{Soil}) and after (I_{SS}) at the *Radioactivity Laboratory* of the *Laboratori Nazionali del Sud* (LNS - INFN) in Catania using a Gamma ray spectrometer with High Purity Germanium (HPGe) detector considering a detection period of 24 h. Leachability of the contaminated soil and the S/S products was examined at different pH values (3, 5, 7) in accordance to Japanese regulations (Ministry of Environment Government of Japan, 2003) (Mallampati et al., 2015). ICP - OES was used for detection Cs levels in the collected leachant, then Cs percentage immobilisation was calculated for all S/S samples. All tests were carried out in triplicate and mean values were shown.

3. Results and discussion

3.1 γRS index assessment

γRS index of different PC - MG or PC - IP grout mixtures at different PC : SM ratios (S : G = 3 : 1) was obtained as a function of the emission energy and results are given in Figure 1. It can be seen that γRS depends on the energy of the photon that interacts with the material, and presents the highest values (up to 70%) for the lowest energies investigated. The observed high variability was due to the different photon absorption mechanisms involved (photoelectric effect, Compton scattering and pair production). Different peaks were also observed in the γRS variation with the highest value of 35 and 42%, corresponding to the energy of ~300 keV, for MG and IP grouts, respectively. This depends on the irregular influence of the materials constituting the grout mix on the shielding features (Akkurt et al., 2010; Chanthima et al., 2012). A higher increasing in γRS index with SM amount increasing was also observed for energies higher than 300 keV in the case of PC - IP mixtures respect to PC – MG ones, due to their higher shielding features.

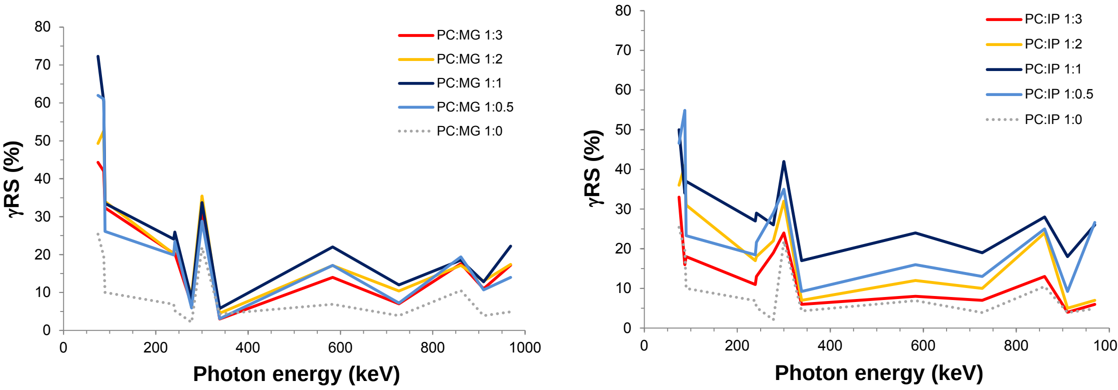

Figure 1: γRS variation as a function of the photon decay energy for different PC:MG (a) and PC:IP (b) ratios (S:G 3:1).

Average γRS and γRS$_{662}$ (corresponding to the main γ-ray emission energy of ^{137}Cs =662 keV) were also reported against the percentage amount of SM used (Figure 2).

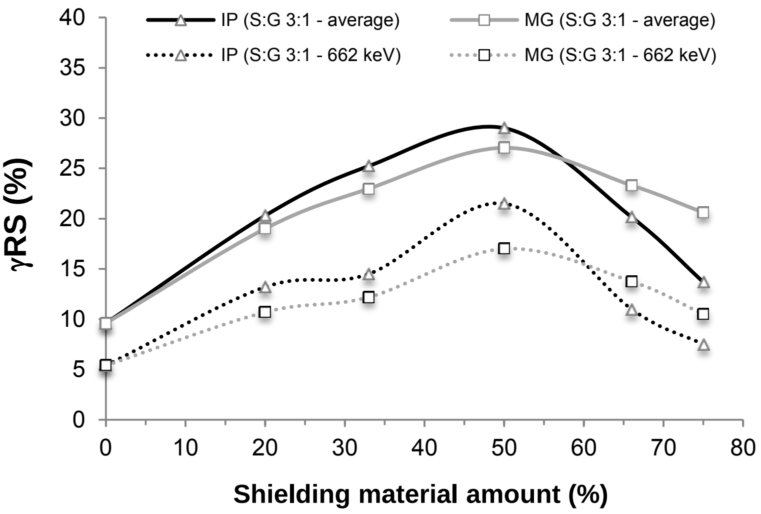

Figure 2: γRS variation as a function of the shielding material amount for MG and IP mixtures

The replacement of PC with MG or IP resulted in a marked increase in the γRS index up to its maximum value which corresponded to a SM percentage of 50%. Maximum γRS average values of ~27 and ~29% were obtained for MG and IP grouts, respectively, whereas γRS$_{662}$ of ~17 and ~21% were found for the same mixtures. Overall, this corresponded to a γRS index increase up about 4-fold respect to the case with PC only. A further SM addition decreased the γRS values, resulting in a consequent worsening of the shielding performance. This behaviour strictly reflected the variation of the final density measured for the S/S mixes (Ouda, 2015), which decreased for SM amounts higher than 50% due to the negative effect of the inert materials addition on the PC hydration process (Akkurt and El-Khayatt, 2013). Due to the highest γRS values observed, the PC : SM ratio of 1 : 1 was selected for the further experimental investigation of this work, aimed at assessing the influence of grout amount percentage on S/S performance. An increase in γRS was also observed with increasing the grout amount in S/S soil grouts for both the SM investigated (Figure 3).

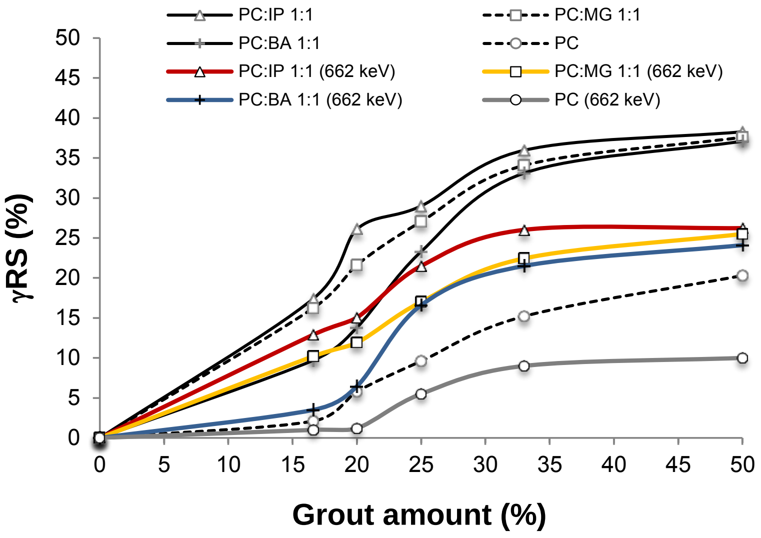

Figure 3: γRS variation as a function as a function of the grout amount for MG and IP mixtures.

The higher γRS index values were found in the case of MG and IP addition respect to BA and PC, following the order IP>MG>BA≫PC, with the most marked difference in γRS of about 20% observed for the minimum S : G ratio. At the ^{137}Cs emission energy (662 keV), γRS of IP - mixtures increased to 12.9, 15.1, 21.5 and 26.0% for increasing grout percentages of 16.6, 20.0, 25.0 and 33.0%, respectively. A further increase in the grout percentage had no significant effects on the γ-shielding performance. This is clearly related to the influence of density variation on γRS, and fixes a threshold that must be considered in scaling-up and design activity for a cost-effective S/S remediation of ^{137}Cs-contaminated soils.

3.2 Immobilisation of Cs in stabilised/solidified matrices

Cs immobilisation was observed in the range 81.1 - 86.7% for the soil samples S/S with PC only (Table 2) probably due to the formation of insoluble complex (Cs aluminosilicates jointly with the formation of silicate hydrates capable to entrap Cs ions) (Papadokostaki and Savidou, 2009).

Table 2: Cs - immobilization (%) from elution tests

G	S:G	G (%)	pH	Cs immobilisation (%)
PC	3:1	25	7	81.1±3.1
PC	2:1	33.3	7	85.7±1.2
PC	1:1	50	7	86.7±1.7
PC:MG 1:1	3:1	25	7	89.4±6.4
PC:MG 1:1	2:1	33.3	7	92.7±3.4
PC:MG 1:1	1:1	50	7	97.8±2.1
PC:MG 1:1	3:1	25	5	88.8±5.0
PC:MG 1:1	2:1	33.3	5	91.1±4.9
PC:MG 1:1	1:1	50	5	96.0±2.2
PC:MG 1:1	3:1	25	3	88.1±6.4
PC:MG 1:1	2:1	33.3	3	89.7±1.7
PC:MG 1:1	1:1	50	3	92.2±0.9
PC:IP 1:1	3:1	25	7	88.2±3.3
PC:IP 1:1	2:1	33.3	7	89.1±2.6
PC:IP 1:1	1:1	50	7	90.6±1.9

When MG was used, up to 97.8% of the total Cs was immobilised. The decrease in leaching rate with MG addition can be attributed to its fine texture and high surface area, capable of reducing the porosity of S/S matrix respect to the treatment using PC only, by means of the refinement in pore structure, and increasing its contaminant adsorption capability (Papadokostaki and Savidou, 2009). This is in agreement with Evans (2008) who reported that high-density concrete showed a preferential sorption of Cs on high-density fine aggregates and with El-Kamas et al. (2002). Higher immobilisation found for the sample S/S with the MG - PC grout is also due to the larger Cs adsorption capacity of magnetite observed at higher pH values, which characterised S/S materials. The MG adsorption increase with pH resulted from two possible mechanisms: an increase in the sites available for metal ions adsorption and increasingly more negatively charged and thus more electrostatically attractive surface to the Cs^+ cations (Ebner et al., 2001).Lower immobilisation percentages obtained in the case of IP addition were due to the low specific area of IP and highlight the key role of adsorption processes in contaminant leaching phenomena. Results also showed that in PC - MG based S/S treatment, even in low pH conditions (pH: 3, 5), a good immobilisation (88.1 – 96.0%) was achieved. Good Cs immobilisation achieved in the presence of MG also depended on the positive dependence of the MG adsorption capacity with pH and its high adsorption capability even at pH values close to zero. This was possible because of the relatively large ionic size of Cs^+ ions and their interaction with the first sheath of water molecules that covers the ions and normally forbids metal ions from making direct contact with MG surface sites (Ebner et al., 2001).

4. Conclusions

The replacement of Portland cement by magnetite or iron powder (up to 50%) results in a marked increase in the S/S γ-radiation shielding performance, up to about 4-fold respect to the case with cement alone. A further addition results in a worsening of the shielding performance, due to the reduction of the density of the S/S mixtures.

In general, γRS index increases with increasing the grout amount in S/S soil mixture, with the highest values observed in the case of iron powder addition, following the order iron powder > magnetite > barite powder $\gg$ Portland cement. Specifically, at the ^{137}Cs emission energy of 662 keV, γRS of IP - mixtures increased to 12.9, 15.1, 21.5 and 26.0% for increasing grout percentages of 16.6, 20.0, 25.0 and 33.0%, respectively. A further increase in the grout percentage does not have important effect on the γ-shielding performance increase. This fixes a potential threshold that must be considered in scaling-up and design activities for a cost-effective S/S remediation of ^{137}Cs-contaminated soils.

The use of magnetite - grouts permits reaching the highest Cs - immobilisation of 97.8%, due to the magnetite fine texture and high specific area, capable of reducing the porosity of S/S matrix respect to the treatment using iron powder or cement alone. A high immobilisation of (88.1 - 96.0%) is achievable also in low pH conditions (pH: 3, 5) due to the positive dependence of the magnetite adsorption capacity with pH and its high adsorption capability even at pH values close to zero. The high γ-shielding performance of magnetite - PC mixtures, slightly lower than those of iron powder-PC ones, jointly with the immobilisation performance, reveal magnetite - PC mixtures as the best choice, highlighting the possibility of their employment in S/S treatment. This is really encouraging, considering the perspective of in situ treating radioactive Cs - contaminated soils.

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