Three-year performance of in-situ solidified/stabilised soil using novel MgO-bearing binders

Fei Jin*, Fei Wang, Abir Al-Tabbaa

Department of Engineering, University of Cambridge, Trumpington Street, Cambridge, CB2 1PZ, UK

HIGHLIGHTS

- MgO-bearing cements were investigated in a full scale field S/S trial.
- The effects of inorgano-organo-clay and binder content were investigated.
- Long-term performance of cores was evaluated by UCS and leaching properties.
- The MgO-GGBS blends showed superior performance compared to other binders.

ARTICLE INFO

ABSTRACT

A new group of MgO-bearing binders has been developed recently which showed improved sustainability and technical performance compared to Portland cement (PC). However, the application of these MgO-bearing binders in the Solidification/Stabilisation (S/S) techniques is very limited. This study investigates the three-year performance of a highly contaminated soil treated by in-situ S/S using MgO-bearing binders and PC. The core quality, strength, permeability and the leaching properties of the S/S materials were evaluated. The effects of binder composition, addition of inorgano-organo-clay (IOC) and the grout content on the properties of the 3-y S/S materials are discussed. It is found that although MgO alone provided negligible strength to the soil, it is superior in immobilising both inorganic and organic contaminants. Replacing MgO by ground granulated blast-furnace slag (GGBS) significantly enhanced the strength while also performed well in immobilising the contaminants. The improved pH buffering capacity was attributed to the low solubilities of brucite and hydrotalcite-like phases formed in the MgO-bearing binders, and was also the reason for the improved performance in stabilising contaminants. The addition of IOC slightly decreased the strength and the permeability of the S/S materials but inconsistent effect on the contaminant immobilisation was found depending on the binder composition. This study showed no degradation of the S/S materials after 3 y exposure to field conditions and has proved the applicability and the advantages of MgO-bearing binders over PC in S/S.

1. Introduction

Solidification/stabilization (S/S) is a commonly used land remediation method, which aims to enhance the mechanical properties and leaching resistance of the contaminated soil using various binders. Portland cement (PC) is the most widely used binder in the S/S techniques. However, PC production is known to be highly energy intensive and responsible for 5–10% anthropogenic CO_2 emissions, leading to various measures to reduce its usage. Additionally, the high pore water pH of PC (usually >13) will increase the mobility of many heavy metals (Conner, 1990). When the contaminants are not limited to inorganics, PC is known to be ineffective and must be applied with strict caution (Pollard et al., 1991). The replacement of PC by industrial by-products (e.g. fly ash and slag) is widely accepted due to the reduced environmental impact and improved material properties such as lower permeability, better buffering capacity and reduced leachability (Weng and Huang, 1994; Dermatas and Meng, 2003). Additionally, the residual carbon content in fly ash plays a significant role in adsorbing organic contaminants, reducing their mobility as reported in (Low and Batley, 1988; Banerjee et al., 1995). Industrial adsorbents such as activated carbon and inorgano-organo-clays

(IOC) also received significant attention and have shown promise for immobilising organics in the S/S techniques (Pollard et al., 1991) but their long-term effect on the final waste forms and their compatibility with different binder formulations have yet to be validated.

Magnesia (MgO) has been reported to have superior immobilisation capacities for a wide range of contaminants due to (1) its pH neutralisation range of 9–11, where the solubility of metal hydroxides are at their minimum; (2) ion-exchange between magnesium and other metal cations and (3) complexation between contaminants and OH-groups on the MgO surface (García et al., 2004; Rötting et al., 2006; Cubukcuoglu and Ouki, 2012; Tresintsi et al., 2013). In addition to numerous studies (Bochkarev et al., 2007; Nagappa and Chandrappa, 2007; Moussavi and Mahmoudi, 2009) on the wastewater treatment using MgO, a few studies (García et al., 2004; Iyengar, 2008; Suzuki et al., 2013; Wang et al., 2015a) have been carried out on the utilisation of MgO for contaminated land remediation. They concluded that MgO is an effective immobilisation agent for soils contaminated by heavy metals and the efficiency can last for a long time due to the low solubility of its hydration product (Mg(OH)$_2$, brucite). Recently, a new group of MgO-bearing cements has been developed (Al-Tabbaa, 2013), which combines PC, MgO and other industrial by-products (mainly fly ash or slag) in the formulations and showed many technical and sustainability advantages over conventional PC. Iyengar (2008) investigated the performance of MgO and pulverised fly ash (PFA) blend in the treatment of Zn contaminated soil. It is found that the leached Zn concentration was significantly lower in MgO-PFA blend than in PC-PFA blend, although the strength of the former was much lower due to little reaction between MgO and PFA (Iyengar, 2008). Jin and Al-Tabbaa (2014) compared the performance of MgO-ground granulated blastfurnace slag (GGBS) and lime-GGBS blends in the presence of high levels of Pb and Zn contaminations. They reported an improved pH buffering capacity and higher immobilisation efficiency of the former binder due to the hydrotalcite (Mg$_6$Al$_2$CO$_3$(OH)·4(H$_2$O))-like phases formed. Apart from the laboratory work, a field study showed that although using MgO alone produced minimum strength, it is very effective in immobilising both organic and inorganic contaminants (Wang et al., 2015a). Replacing 90% of MgO by GGBS not only maintained the metal immobilisation efficiency but also significantly enhanced the strength (Wang et al., 2015b).

This study aims to further validate the utilisation of MgO-bearing binders in S/S techniques by evaluating the performance of samples cored from a highly contaminated land after 3 y of in-situ S/S treatment. The main objectives are threefold: (1) investigating the long-term mechanical and leaching performance of S/S materials; (2) comparing various MgO-bearing binders with PC; and (3) assessing the effect of IOC on the properties of S/S materials.

2. Materials and methods

2.1. Contaminated site and soil characterisation

The contaminated site characterisation can be referred to Wang et al. (2015a). The S/S treatment was performed in May 2011 by in-situ soil mixing down to 4 m below ground level, and the soil is primarily composed of made ground. The water content of the soil is ~25%, and the liquid limit and plastic limit are ~30% and ~24%, respectively. According to the chemical analysis performed in 2010, the main heavy metal contaminants are Pb (38 mg kg^{-1}), Zn (99 mg kg^{-1}), As (128 mg kg^{-1}), Cr (495 mg kg^{-1}), Cu (823 mg kg^{-1}) and Ni (806 mg kg^{-1}). The primary organic contaminants are diesel range total petroleum hydrocarbons (TPH) (1960 mg kg^{-1}) and semi-volatile semivolatile organic compounds (SVOCs) including

chloro-nitro-benzenes (1365 mg kg^{-1}), chloro-methyl-nitro-benzenes (222 mg kg^{-1}), and chloro-aniline isomers (58 mg kg^{-1}). Nevertheless, it should be noted that the contamination levels are highly variable depending on the location in addition to the varying nature of the site soil itself. According to the official data (Defra, 2015), the annual rainfall in this region is ~600 mm and the temperature varies from 1 to 21 °C across the year. The average pH value of the rain is 4.4–6.1.

2.2. Materials and sampling

Although a wide range of binder compositions were applied at the site, only those containing MgO were cored at 3 y for detailed study together with PC (CEM I) for comparison purpose. The mixes assessed in this study were listed in Table 1, where it can be seen that three groups of MgO-bearing binders were utilised, namely, MgO alone, MgO-GGBS, and CEM I-MgO-PFA cements. The IOC was prepared in the laboratory by modifying bentonite with chlorhydrol and polypropylene glycol (PPG), the composition of which is detailed in Wang et al. (2015b). The effects of binder composition, addition of IOC and the grout content were investigated according to the mix design. The site sampling was performed in March, 2014 using the pressurised rotary coring down to 1.5 m for most mixes while two mixes (2 MG and MG + IOC) were cored down to 3 m. The core samples were sealed in the Ø 0.1 × 1.5 m plastic tubes and sent to the laboratory for testing.

2.3. Testing procedure

The qualities of the core samples were firstly assessed by total core recovery (TCR) and rock quality designation (RQD) calculated as follows:

$$TCR = \frac{l_p}{l_t} \times 100\%$$

$$RQD = \frac{l_{100}}{l_t} \times 100\%$$

where l_p is the sum of length of core pieces, l_{100} the sum of length of core sticks longer than 100 mm measured along the centre line of the core and l_t the total length of the core.

To determine the unconfined compressive strength (UCS), the cores were trimmed into cylindrical pieces with a height to diameter ratio of ~2. The permeability test was conducted in a triaxial cell according to (US Army, 1992) using trimmed cylinders with a height to diameter ratio of ~1. After the UCS test, the crushed samples were then subjected to the batch leaching procedure as per BS EN 12457-2 (2002). The CO$_2$ saturated water (pH at ~5.6) was used instead of deionised water to simulate the slightly acidic rainwater. The concentrations of the major heavy metal contaminants (Pb, Zn, As, Cr, Cu and Ni) as well as Al, Si, Ca and Mg in the leachate were analysed using inductive couple plasma optical emission spectroscopy (ICP-OES) on the PerkinElmer 7000 machine. An accurately measured 300 mL leachate was then transferred into a 1000 mL plug-contained conical flask for organic extraction. After adding 30 mL dichloromethane (DCM) into the flask and shaking for 2 min, the mixture was left until a clear separation of two layers was observed. The bottom layer was carefully dripped into a cylinder. After repeating this extraction three times, the collected mixture was poured into a pre-weighted glass container, which was then put in a fume cupboard. After 72 h evaporation, the mass of the residual was recorded and calculated for the total organics (TO) concentration in the leachate (Wang et al., 2015b).

Table 1
Binder compositions used in the S/S treatment.

Mix denotation	Binder			Binder components ratio	Total slurry content (wt%)	Water:cement:modified clay
C	CEM I				15	1:1:0
M	MgO				15	1:1:0
M + IOC	MgO				22.5	1:1:1
MG	MgO	GGBS		1:9	15	1:1:0
2 MG	MgO	GGBS		1:9	30	1:1:0
MG + IOC	MgO	GGBS		1:9	22.5	1:1:1
CMF	CEM I	MgO	PFA	1:4:5	15	1:1:0
CMF + IOC	CEM I	MgO	PFA	1:4:5	22.5	1:1:1

3. Results

3.1. Core quality

The qualities of the retrieved cores vary significantly depending on the binder composition. To quantify the quality of the core recovered from the boreholes after S/S treatment using different binders, TCR and RQD of each core were calculated and shown in Fig. 1. In general the two parameters agreed well with each other except for M + IOC mix, which has a high TCR but very low RQD. This can be attributed to the very low but consistent strength of this mix. According to the RQD classification (Deere, 1989), mixes containing only MgO (M, M + IOC) were of very poor quality (RQD < 25%), while only one mix with 2 times grout content of MgO + GGBS exhibited good quality cores (RQD = 75–90%) with the others in between.

3.2. Strength and permeability

Fig. 2 shows the UCS of the trimmed cylinders from each core with depth. It can be seen that soils treated with MgO only showed minimum strength as low as 200 kPa, while binders made of MgO and GGBS (MG, 2 MG and MG + IOC) gained more than 3.5 MPa strength at 3 y. It should be noted that most specifications on the UCS of S/S materials are based on the 28-d strength, but a comparison of the 3-y UCS with the specifications is still worthwhile in the view of assessing the strength degradation of the S/S materials exposed to field conditions. US EPA suggested an UCS of 350 kPa at 28 d for materials to be disposed of to landfill (USEPA, 1996), while in the Netherlands and France, a UCS of 1000 kPa is suggested (Perera et al., 2005b). A much higher value of 3500 kPa has been suggested by Wastewater Technology Center (1991) taking into account that the compaction of municipal waste might subject the S/S material to higher stresses. As can be seen from Fig. 2, only the mixes using MgO and GGBS can fulfil the requirement in Wastewater Technology Center (1991). In terms of the effects of the variables investigated in this study (binder composition, modified clay addition and grout content), a few conclusions can be drawn from the UCS results: (a) MgO alone is very weak due to the nature of its hydration product (brucite) (Vandeperre et al., 2007); (b) replacing MgO by GGBS enhanced the strength remarkably; (c) doubling the grout content and hence the binder content almost doubled the strength of the treated soil; (d) replacing 90% PC by MgO and PFA had no obvious effect on the strength in the long term since the pozzolanic reaction between PC and PFA contributed to strength (d) adding IOC in the binders generally decreased the strength slightly. These findings agree well with the strength development under various binders reported by Wang et al. (2015a) at 1.5 y.

As for the permeability, in general the binders with higher strengths exhibited lower permeabilities as shown in Fig. 3. The permeability limit was suggested to be 10^{-8} m s^{-1} (Wastewater Technology Center, 1991) for landfill disposal, while lower limit as 10^{-9} m s^{-1} for disposal was specified by USEPA as well as for in-ground treatment (Al-Tabbaa and Evans, 1998) and utilisation (Wastewater Technology Center, 1991). It can be seen that MG and PC binders have permeabilities of less than 10^{-10} m s^{-1}, while CMF binders exhibited permeabilities of ~10^{-9} m s^{-1}. Only one mix (M + IOC) exceeded the limit of 10^{-8} m s^{-1}. Fig. 3 also revealed that the addition of IOC slightly decreased the permeability.

3.3. Batch leaching results

3.3.1. Leachate analysis

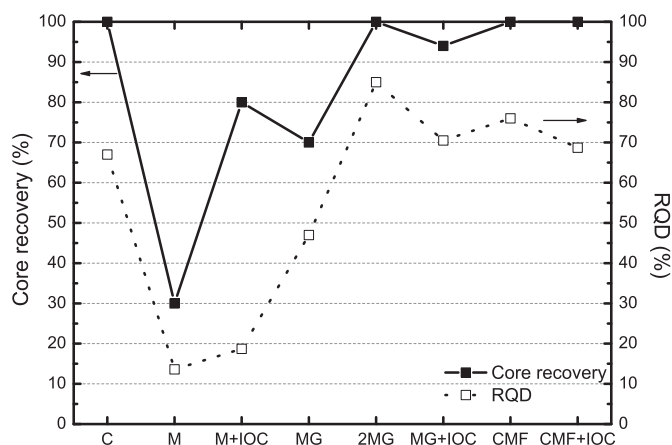The leachate analysis after extraction with carbonic water

Fig. 1. Total core recovery and rock quality designation of the 3-y S/S cores.
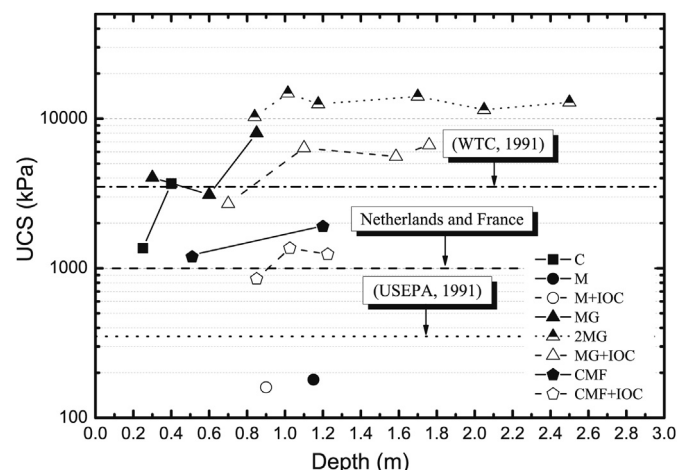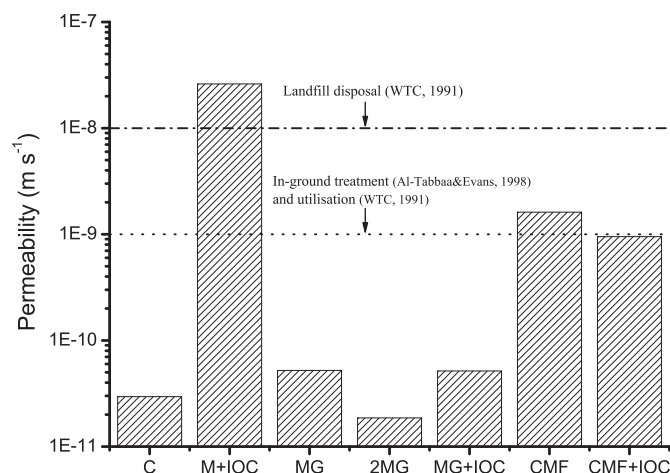

Fig. 2. UCS variation with depth of the 3-y S/S cores.

Fig. 3. Permeability of the 3-y core samples using different binders.

soils. It can be seen that even without treatment, the As leached is less than the limit for inert waste sites. PC is found to have negligible effect on immobilising As, while the other binders showed some improvement but highly dependent on the depth of the samples used, indicating the heterogeneity of the contamination or the poor quality mixing on the site. In general, regardless of the binder composition and depth, all the As concentrations satisfy the requirement for inert waste sites. The effects of grout content and addition of IOC are not clear due to the large variability of the data.

In terms of the leachabilities of Cu and Ni, the results are very similar across all the binders used. The major finding are summarised as follows: (a) PC slightly decreased the leachability of Ni while increased that of Cu after 3 y; both metals exceeded the limits set for inert waste sites; (b) All the MgO-bearing binders decreased the leachabilities of Cu and Ni to lower than limit for inert waste site; (c) There is no apparent effect of doubling the grout content and adding IOC for MG and CMF binders. However, adding IOC into MgO (M + IOC) has significantly increased the leachability of Cu and Ni compared to MgO alone (M), although they are the best-performing mixes.

As for the leachable TO, a notable reduction from over 300 mg L^{-1} to 10–200 mg L^{-1} was observed after S/S treatment (Fig. 4d). All the binders are effective while comparison among them is difficult due to the heterogeneity of the soils. It is noteworthy the no clear relationship was found between pH and TO, which is consistent with (Kogbara et al., 2011).
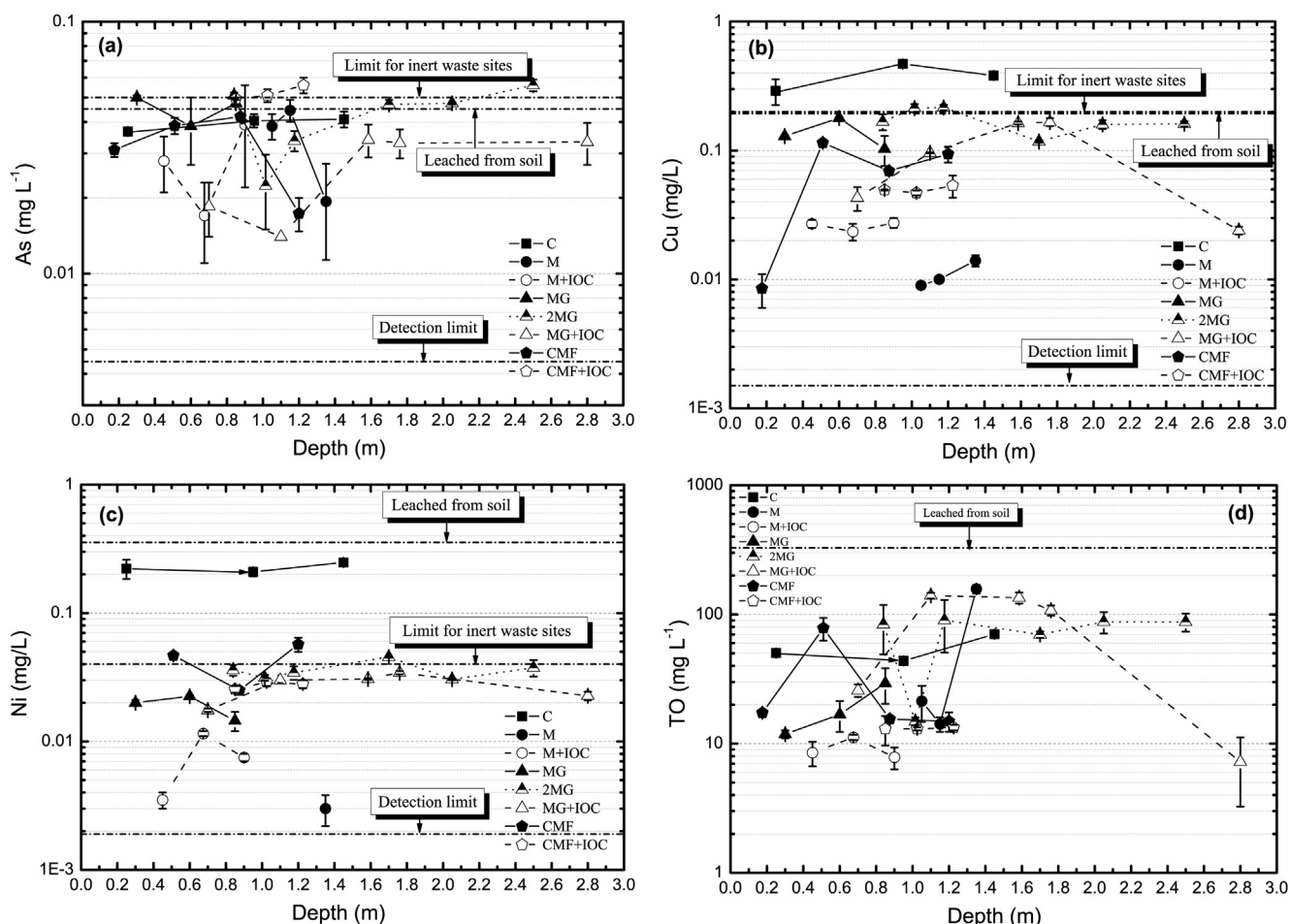
showed that the concentrations of Cr, Cd, Pb and Zn were below the limit of detection (LOD) (0.7, 0.5, 20 and 3.3 μg L^{-1} for Cr, Cd, Pb and Zn, respectively) for all the samples, and are also far below the leaching limits set for the acceptance of inert waste sites in landfills (EA, 2002). The concentrations of three detectable metals, (As, Cu and Ni) and the total leachable organics, were shown in Fig. 4a–d together with those leached from untreated

Fig. 4. Leachate concentrations of the heavy metals and organics for the 3-y cores as a function of depth: (a) As; (b) Cu; (c) Ni and (d) TO.

3.3.2. pH dependent leaching of metals

Fig. 5 shows the concentrations of four cations (As, Cu, Ni and Al) in the leachates as a function of the pH values of the leachates. As can be seen, the pH values of the S/S materials after 3 y of treatment are mostly >9.0 and the binder composition showed the most remarkable impact on the pH. MgO and CMF binders have pH values in a relatively narrow range at ~10.0, which are controlled by the solubility of brucite due to the large amount of MgO present. PC treated soils presented pH values from 9.0 to 10.5, which is far less than the equilibrium pH of portlandite (~12.5), indicating that significant carbonation occurred after 3 y of curing in the field. Mixes using MgO and GGBS (MG, 2 MG, MG + IOC) exhibited pH in the range of 7.5–11.5, with most of the values lying between 10.5 and 11.5. The high pH values are attributed to the high pH buffering capacity of the hydrotalcite-like phases formed in these blends (Jin and Al-Tabbaa, 2014). In addition, since the formation of hydrotalcite-like phases would become more prominent with curing ages, the buffering capacities of MG blends would improve with aging (Iyengar, 2008). The three very low pH values belong to the MG + IOC binder, which could be due to the low binder content in the samples tested due to the poor mixing. No apparent effects of IOC and grout content on the pH values were observed.

As for the electrical conductivity (EC) of the leachates, they decreased in the order of C (2570 ± 270 μS m^{-1}) > CMF (2130 ± 819 μS m^{-1}) ≈ M (1940 ± 156 μS m^{-1}) > M + IOC (1860 ± 321 μS m^{-1}) ≈ CMF + IOC (1810 ± 70 μS m^{-1}) > MG (1520 ± 148 μS m^{-1}) > 2 MG (1200 ± 211 μS m^{-1}) > MG + IOC (813 ± 202 μS m^{-1}). Apparently, for the same binder, the addition of IOC decreased the EC and the replacement of PC/MgO by industrial by-products (GGBS/PFA) also decreased the EC. These can be attributed to the excellent adsorption capacities of ionic substances onto the modified clay and GGBS/PFA (Montgomery et al., 1991; Dermatas and Meng, 2003).

From Fig. 5a–c, it can be seen that the leachabilities of As, Cu and Ni are not pH dependent as reported by the literature (Johnson et al., 1996; Halim et al., 2004; Kogbara et al., 2011). Instead, the binder composition is the most important factor that governs the leachabilities of these contaminants, suggesting different immobilisation mechanisms involved. In contrast, Al leachability is strongly pH-dependent for all the binders (Fig. 5d).

The leaching results for As include both As (III) and As (V). According to Stronach et al. (1997) and Vandecasteele et al. (2002), As (III) and As (V) solubility during S/S was limited by the formation of the sparingly soluble CaHAsO$_3$ and Ca$_3$(AsO$_4$)$_2$ phases, respectively, which are both pH-dependent. However in this study, negligible As was leached and pH-dependence was not observed (Fig. 5a), suggesting other immobilisation mechanisms in control, e.g. adsorption, isomorphic substitution. In addition, it is postulated that As can also be incorporated in the C–S–H matrix and form iron arsenate precipitate (Halim et al., 2004), which could explain the low leachability of As after S/S treatment.

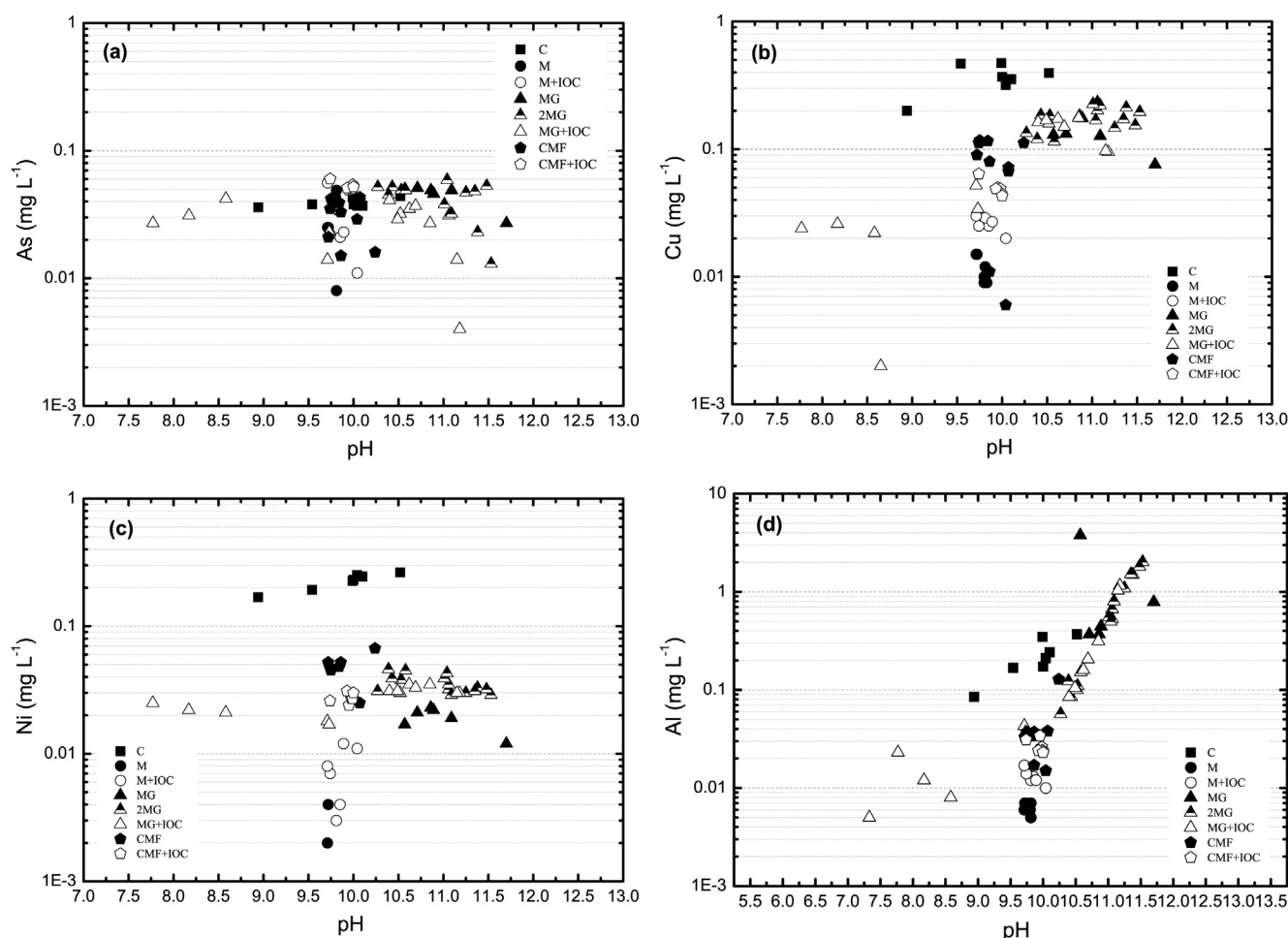In general, the trends of leachability of Cu and Ni in soils treated

Fig. 5. Concentrations of (a) As, (b) Cu, (c) Ni, and (d) Al in the leachates as a function of pH.

by different binders are very similar, which increased in the order of: M and M + IOC ≤ CMF and CMF + IOC ≈ MG, 2 MG and MG + IOC < C (Fig. 5b and c). The concentration of Cu in the leachate is reported to be controlled by the solubility of $Cu(OH)_2$ and malachite ($Cu_2(OH)_2CO_3$) (Kogbara and Al-Tabbaa, 2011; Komonweeraket et al., 2014). However, it is also found that Cu is likely to form strong complexes with organic ligands in the soils (Johnson et al., 1996; Rieuwerts et al., 1998), resulting in higher leachability, which would be more applicable to this study due to the high concentrations of organic matters present in the contaminated soils. Kogbara et al. (2011) stated that $NiCO_3$ is the solubility-controlling phase for Ni in the lime-slag and PC-slag treated soils, but this study shows that for different binder systems and under field conditions, more complex phases are likely to be present and control the leachability of Ni. For example, isomorphic substitution took place when Mg–Al hydrotalcite was used to remove Ni from wastewater (Liang et al., 2013), which could explain the marginal leachability in all of the MgO-GGBS binders (Fig. 5c). Unlike the contaminants, Al is significantly pH controlled, which agreed well with the literature that Al is determined by the solubility of $Al(OH)_3$ in both PC and hydrotalcite systems (kumar Allada et al., 2002; Wu et al., 2013; Komonweeraket et al., 2014).

Fig. 6 shows the relationships between Ca/Mg and Si concentrations in the leachates of the S/S samples. It is very clear that the concentrations and relationships are strongly dependent on the binder composition. In mix C, the Ca concentration is mainly controlled by portlandite, which is one of the major hydration products of PC, as well as calcite due to carbonation. On the other hand, the Mg concentration is dominated by the solubility of brucite, which originates from the PC impurity (Taylor, 1997).

In the mixes with only MgO as the binder, significantly lower concentrations of Ca and Si and higher concentrations of Mg were found after leaching test. The source of Ca and Si is probably from the soil itself as well as the impurities in the MgO used (Jin and Al-Tabbaa, 2013), while the Mg concentration is controlled by both the solubilities of MgO (unhydrated) and brucite. It is also found that the addition of IOC in the MgO slightly increased the Si concentration leached, which is attributed to the dissolution of the modified bentonite at high pH (Rozalen et al., 2009). The same effect of IOC on the leaching of Si was not found in other binders due to the presence of C–S–H, which dominates the leaching of Si, as will be discussed in the following.

The range of Ca/Si ratio leached from the CMF and CMF + IOC mixes is around 0.8–2.0. Meanwhile, significantly higher concentrations of Mg were detected due to the presence of brucite. It is also well known that decalcification of the C–S–H gel occurs with carbonation, resulting in the decrease of Ca/Si ratio and the formation of calcite. Thus, the concentrations of Ca and Si leached from CMF mixes are probably controlled by the solubility of both calcite and C–S–H.

In mixes of MG, 2 MG and MG + IOC, there are more Si and less Ca leached compared to mix C, which is due to that the main hydration products are C–S–H and hydrotalcite like-phases (Jin et al., 2013, 2014), with much less portlandite and calcite formed. A strong positive linear correlation was found between Mg and Si concentrations indicating the formation of magnesium silicate hydrate (M-S-H) gels, which is in agreement and confirms the findings in previous studies on the MG mixes (Jin et al., 2013, 2014; Jin and Al-Tabbaa, 2014). The Mg concentration increased significantly faster than Si concentration, indicating other solubility-controlling phases, which are hydrotalcite-like phases, one of the major hydration products in the MG mixes containing brucite layers in its structure (Jin et al., 2014). kumar Allada et al. (2002) reported that the solubility of hydrotalcite-like phases is controlled by the individual hydroxide component in their structures and thus the Mg concentration is mainly controlled by the solubility of brucite.

4. Discussion

4.1. Replacement of PC by MgO in the PC-PFA mix in soil remediation

The replacement of PC by PFA has been investigated extensively considering the enhanced sustainability and durability in the long term (Taylor, 1997). In the S/S treatment, PFA is reported to be an effective adsorbent for many heavy metals (Wang and Wu, 2006) and in particular organic contaminants (Banerjee et al., 1995). The replacement of PC by MgO has been studied by Vandeperre et al. (2008), showing decreased mechanical properties due to the weak nature of brucite and the minimal reaction between brucite and PFA. The results in this study are consistent with the previous works on the PC-MgO-PFA cement blends; however, in the context of soil remediation, this blend performed satisfactorily in terms of strength and permeability at 3 y (Figs. 2 and 3). In addition, due to the pH buffering capacity of MgO, it is found that the pH values of the leachates have been confined in a much narrow range compared to PC (Fig. 5). Accordingly, the leached Cu, Ni and total organic content are significantly lower than those from PC.
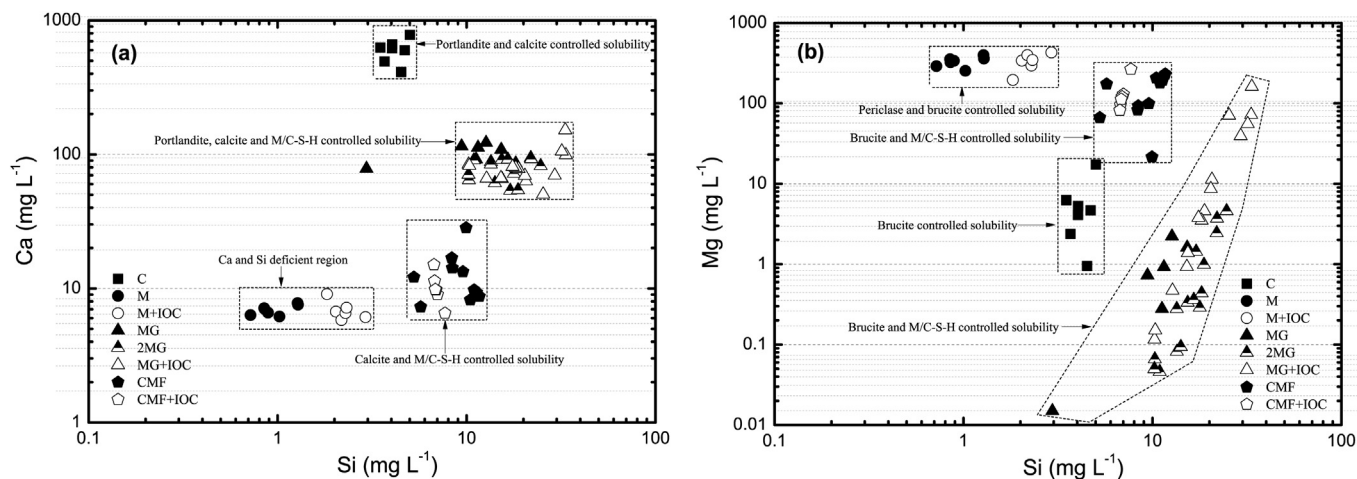

Fig. 6. The relationship between the concentrations of (a) Ca and Si, (b) Mg and Si in the leachates of the 3-y S/S cores.

Nevertheless, whether the improved immobilisation efficiency should be attributed to the PFA or the MgO is not clear.

4.2. Innovative MgO and MgO-GGBS binders in soil remediation

As reviewed in the introduction, the use of MgO in the soil remediation has been successfully applied and showed promising results (García et al., 2004; Iyengar, 2008; Suzuki et al., 2013; Wang et al., 2015a). The current study agreed well with the literature that MgO alone can serve as an efficient immobilising agent in the contaminated soils. The concentrations of the leached metals are the least among all the binders tested, although the strength is far below the requirement for S/S materials. The replacement of MgO by 90% GGBS not only reduced the cost and enhanced the sustainability but also remarkably improved the strength, as can be seen in Fig. 2. This innovative binder has recently gained more and more attention due to its better mechanical properties in the long term and its improved immobilisation capacity on Pb and Zn compared to the commonly used lime-GGBS binder (Yi et al., 2013; Jin et al., 2014; Jin and Al-Tabbaa, 2014). The hydrotalcite-like phases formed in this binder have been extensively studied as promising adsorbents for numerous heavy metals and organics (You et al., 2002; Liang et al., 2013). However, no reports on the application of hydrotalcite-like phases for the remediation of heavy metal contaminated soil are available. The current study provided valuable information regarding the performance of MgO-GGBS binder in the soil remediation after a relatively long time (3 y). The results are very promising in terms of higher strength, similar permeability and better immobilisation efficiency for both organic and inorganic contaminants compared to PC.

4.3. Effect of IOC in soil remediation

It is reported that the addition of clay could adversely affect the strength of cement pastes partially due to the swelling properties of the clay in water, which removed the water required for cement hydration, and partially due to the effect of the clay itself on cement hydration (Montgomery et al., 1991). This study is in agreement with the literature and showed that this adverse effect is also found on various MgO-bearing binders (Fig. 2), although a slight decrease of permeability was observed probably due to the swelling properties of IOC. In terms of stabilisation of contaminants, the effect of IOC is not consistent across the binders and contaminants. Taking Cu as an example, adding IOC in CMF and MG mixes decreased the leachable Cu while increased it in binder M (Fig. 4b). As for the organics, IOC seems to be more effective with binder M instead of CMF and MG. It is therefore inconclusive about the effect of IOC in the MgO-bearing binders and further research is required to elucidate the interaction among IOC and various MgO-bearing binders and the contaminants.

4.4. Time-dependent performance of different binders in soil remediation

It is known that real-time field validation of S/S techniques is essential, as this is the only exact method of knowing the performance over time, which also provides information for the back analysis of modelling work (Perera et al., 2005a). However, despite the widespread use of S/S techniques, evidence of validation, especially the time-related material performance in the field is still very limited. Particularly for innovative binders used in S/S techniques, real-time field validation will provide the most valuable evidence and help to gain confidence on the binders developed. The strength and leaching properties of selective mixes from the same project have been reported in Wang et al. (2015b) and a confidential

report. The comparison of the 28-d and 3-y data showed consistently increased UCS, decreased total heavy metals and total organics leached from both PC and MgO-containing binders. Thus it is concluded that there is no degradation of the S/S materials after 3 y exposure to the field conditions. However, as is inferred in Chen et al. (2009) that atmospheric carbonation can degrade cement-based solidified wastes and increase the release of heavy metals to the environment with time. It is likely to happen after 3 y considering the decreased pH buffering capacity of the PC-based binders as shown in Fig. 5. On the other hand, MgO-bearing binders showed improved pH buffering capacity due to the low solubility of brucite as well as the hydrotalcite-like phases, ensuring stable immobilisation performance for heavy metals even after a long time. As deduced in Suzuki et al. (2013), MgO treatment at a 5 mg g^{-1}-dry soil dosage is able to provide the soils with an adequate acid buffer capacity to accommodate 100 y of exposure to acid rain at pH 4.0. Therefore, it is indicated that the MgO-bearing binders can serve as promising S/S binders providing better mechanical and immobilisation performance and improved durability and sustainability compared to PC.

5. Conclusions

The performance of 3-y old S/S materials was evaluated in terms of their strength, permeability and leaching properties. The main focus of this study is the innovative MgO-bearing binders introduced for the first time in the application of in situ soil remediation. The results showed that MgO-bearing binders are very promising binders in the S/S techniques, and their properties vary widely depending on their compositions. The major conclusions drawn from the present study are as follows:

(a) The MgO alone provided negligible strength to the soil, but it significantly improved the immobilisation capacities on both the organic and inorganic contaminants;

(b) The replacement of MgO by 90% GGBS increased the strength and decreased the permeability remarkably, achieving >3.5 MPa. UCS and <10^{-10} m s^{-1} permeability at 3 y;

(c) The pH of the leachates follows the order of: MgO + GGBS > MgO ≈ PC + MgO + PFA ≥ PC. The improved pH buffering capacity in the MgO-bearing binders is attributed to the low solubility of brucite and hydrotalcite-like phases formed;

(d) The immobilisation mechanisms for heavy metals are much more complex due to the mixed contamination in the field and the use of novel binders. Further investigations on the detailed microstructural and speciation analysis would be useful to improve the accuracy of modelling;

(e) Al is mainly controlled by the solubility of Al(OH)$_3$ while Mg, Ca and Si are strongly dependent on the binder composition. MgO-bearing binders showed much less Ca leached and Mg concentration is mainly controlled by the solubility of brucite. The Si concentration is not only governed by C–S–H but also M–S–H dissolution in the MgO + GGBS blends;

(f) The effect of IOC slightly decreased the strength and permeability of MgO-bearing binders, but its effect on the contaminants is not clear. Further studies on the interaction among IOC, MgO-bearing binders and contaminants are required;

(g) No degradation in the performance of S/S materials was observed by comparing 28-d and 3-y data. However, the reduced pH values of PC indicated the deterioration to some extent (reduce acid buffering capacity) but will need to be confirmed by further studies on older samples. On the other hand, the high pH buffering capacities of MgO-bearing

binders are likely to ensure a better durability in the long term.

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References

Al-Tabbaa, A., Evans, C.W., 1998. Pilot in situ auger mixing treatment of a contaminated site Part I: treatability study. Proc. ICE Geotech. Eng. 131, 52—59.

Al-Tabbaa, A., 2013. In: Pacheco-Torgal, F., et al. (Eds.), Reactive Magnesia Cement. Book Chapter in Eco-efficient Concrete. Woodhead.

Banerjee, K., Cheremisinoff, P.N., Cheng, S.L., 1995. Sorption of organic contaminants by fly ash in a single solute system. Environ. Sci. Technol. 29, 2243—2251.

Bochkarev, G.R., Pushkareva, G.I., Rostovtsev, V.I., 2007. Intensification of ore concentration and sorption extraction of metals from technogenic raw material. J. Min. Sci. 43, 331—340.

BS EN 12457—2, 2002. Characterisation of Waste—Leaching—Compliance Test for Leaching of Granular Waste Materials and Sludges. British Standard, UK.

Chen, Q.Y., Tyrer, M., Hills, C.D., Yang, X.M., Carey, P., 2009. Immobilisation of heavy metal in cement-based solidification/stabilisation: a review. Waste Manag. 29, 390—403.

Conner, J., 1990. Chemical Fixation and Solidificaton of Hazardous Wastes. Van Nostrand Reinhold, New York.

Cubukcuoglu, B., Ouki, S.K., 2012. Solidification/stabilisation of electric arc furnace waste using low grade MgO. Chemosphere 86, 789—796.

Deere, D.U., 1989. Rock Quality Designation (RQD) after 20 Years. US Army Corps Engrs Contract Rep. GL-89—1. Vicksburg, MS Waterw. Exp. Stn.

Defra, UK, http://uk-air.defra.gov.uk/networks/network-info?view=precipnet. (accessed 10.08.15.).

Dermatas, D., Meng, X., 2003. Utilization of fly ash for stabilization/solidification of heavy metal contaminated soils. Eng. Geol. 70, 377—394.

Environmental Agency, 2002. Guidance on National Interim Waste Acceptance Procedures. Version 1.2 External Consultation Draft. UK.

García, M.A., Chimenos, J.M., Fernández, A.I., Miralles, L., Segarra, M., Espiell, F., 2004. Low-grade MgO used to stabilize heavy metals in highly contaminated soils. Chemosphere 56, 481—491.

Halim, C.E.C., Amal, R., Beydoun, D., Scott, J.A., Low, G., 2004. Implications of the structure of cementitious wastes containing Pb(II), Cd(II), As(V), and Cr(VI) on the leaching of metals. Cem. Concr. Res. 34, 1093—1102.

Iyengar, S.R., 2008. Application of Two Novel Magnesia-based Binders in Stabilisation/Solidification Treatment Systems (PhD thesis). University of Cambridge.

Jin, F., Al-Tabbaa, A., 2013. Characterisation of different commercial reactive magnesia. ICE Adv. Cem. Res. 26, 101—113.

Jin, F., Al-Tabbaa, A., 2014. Evaluation of novel reactive MgO activated slag binder for the immobilisation of lead and zinc. Chemosphere 117, 285—294.

Jin, F., Gu, K., Abdollahzadeh, A., Al-Tabbaa, A., 2013. Effect of different reactive MgOs on the hydration of MgO-activated ground granulated blastfurnace slag paste. J. Mater. Civ. Eng. http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0001009.

Jin, F., Gu, K., Al-Tabbaa, A., 2014. Strength and hydration properties of reactive MgO-activated ground granulated blastfurnace slag paste. Cem. Concr. Compos 57, 8—16.

Johnson, C.A., Kersten, M., Zieglei, 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.

Kogbara, R.B., Al-Tabbaa, A., 2011. Mechanical and leaching behaviour of slag-cement and lime-activated slag stabilised/solidified contaminated soil. Sci. Total Environ. 409, 2325—2335.

Kogbara, R.B., Yi, Y., Al-Tabbaa, A., 2011. Process envelopes for stabilisation/solidification of contaminated soil using lime-slag blend. Environ. Sci. Pollut. Res. Int. 18, 1286—1296.

Komonweeraket, K., Cetin, B., Aydilek, A.H., Benson, C.H., Edil, T.B., 2014. Effects of pH on the leaching mechanisms of elements from fly ash mixed soils. Fuel 140, 788—802.

kumar Allada, R., Navrotsky, A., Berbeco, H.T., Casey, W.H., 2002. Thermochemistry and aqueous solubilities of hydrotalcite-like solids. Science 296, 721—723.

Liang, X., Zang, Y., Xu, Y., Tan, X., Hou, W., Wang, L., Sun, Y., 2013. Sorption of metal cations on layered double hydroxides. Colloids Surf. A Physicochem. Eng. Asp. 433, 122—131.

Low, G.K.C., Batley, E., 1988. Comparative studies of adsorption of polycyclic aromatic hydrocarbons by fly ashes from the combustion of some Australian coals. Environ. Sci. Technol. 22 (3), 322—327.

Montgomery, D.M., Sollars, C.J., Perry, R., Tarling, S.E., Barnes, P., Henderson, E., 1991. Treatment of organic-contaminated industrial wastes using cement-based stabilization/solidification— II. Microstructural analysis of the organophilic clay as a pre-solidification adsorbent. Waste Manag. Res. 9, 113—125.

Moussavi, G., Mahmoudi, M., 2009. Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles. J. Hazard. Mater. 168, 806—812.

Nagappa, B., Chandrappa, G.T., 2007. Mesoporous nanocrystalline magnesium oxide for environmental remediation. Microporous Mesoporous Mater. 106, 212—218.

Perera, A., Al-Tabbaa, A., Reid, J., Johnson, D., 2005a. State of practice report Uk stabilisation/solidification treatment and remediation — part V: long-term performance and environmental impact. In: Al-Tabbaa, A., Stegeman, J. (Eds.), Proceedings of the International Conference on Stabilization/Solidification Treatment and Remediation. Balkema. A.A. Balkema, London, pp. 437—457.

Perera, A., Al-Tabbaa, A., Reid, J., Stegemann, J., Johnson, D., 2005b. State of practice report UK stabilisation/solidification treatment and remediation—Part IV: testing and performance criteria. In: Proceedings of the International Conference on Stabilization/Solidification Treatment and Remediation. Balkema. AA Balkema, London, pp. 415—435.

Pollard, S.J.T., Montgomery, D.M., Sollars, C.J., Perry, R., 1991. Organic compounds in the cement-based stabilisation/solidification of hazardous mixed wastes—mechanistic and process considerations. J. Hazard. Mater. 28, 313—327.

Rieuwerts, J.S., Thornton, I., Farago, M.E., Ashmore, M.R., 1998. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. Chem. Speciat. Bioavailab. 10, 61—75.

Rötting, T.S., Cama, J., Ayora, C., Cortina, J.-L., De Pablo, J., 2006. Use of caustic magnesia to remove cadmium, nickel, and cobalt from water in passive treatment systems: column experiments. Environ. Sci. Technol. 40, 6438—6443.

Rozalen, M., Huertas, F.J., Brady, P.V., 2009. Experimental study of the effect of pH and temperature on the kinetics of montmorillonite dissolution. Geochim. Cosmochim. Acta 73, 3752—3766.

Stronach, S.A., Walker, N.L., Macphee, D.E., Classer, F.P., 1997. Reactions between cement and As(III) oxide: the system CaO—SiO$_2$—As$_2$O$_3$—H$_2$O at 25 °C. Waste Manag. 17 (1), 9—13.

Suzuki, T., Nakamura, A., Niinae, M., Nakata, H., Fujii, H., Tasaka, Y., 2013. Lead immobilization in artificially contaminated kaolinite using magnesium oxide-based materials: immobilization mechanisms and long-term evaluation. Chem. Eng. J. 232, 380—387.

Taylor, H.F.W., 1997. Cement Chemistry. Thomas Telford, New York.

Tresintsi, S., Simeonidis, K., Katsikini, M., Paloura, E.C., Bantsis, G., Mitrakas, M., 2013. A novel approach for arsenic adsorbents regeneration using MgO. J. Hazard. Mater. 265, 217—225.

United States Environmental Protection Agency, 1996. Prohibition on the Disposal of Bulk Liquid Hazardous Waste in Landfills — Statutory Interpretive Guidance (Washington D.C).

US Army, 1992. Test Method for Water Permeability of Concrete Using Triaxial Cell (US).

Vandecasteele, C., Dutré, V., Geysen, D., Wauters, G., 2002. Solidification/stabilization of arsenic bearing fly ash from the metallurgical industry. Immobilization mechanism of arsenic. Waste Manag. 22, 143—146.

Vandeperre, L.J., Liska, M., Al-Tabbaa, A., 2007. Reactive magnesium oxide cements: properties and applications. Sustain. Constr. Mater. Technol. 397—410.

Vandeperre, L.J., Liska, M., Al-Tabbaa, A., 2008. Hydration and mechanical properties of magnesia, pulverized fuel ash, and Portland cement blends. J. Mater. Civ. Eng. 30, 375—383.

Wang, F., Wang, H., Al-Tabbaa, A., 2015a. Time-dependent performance of soil mix technology stabilized/solidified contaminated site soils. J. Hazard. Mater. 286, 503—508.

Wang, F., Wang, H., Jin, F., Al-Tabbaa, A., 2015b. The performance of blended conventional and novel binders in the in-situ stabilisation/solidification of a contaminated site soil. J. Hazard. Mater. 285, 46—52.

Wang, S., Wu, H., 2006. Environmental-benign utilisation of fly ash as low-cost adsorbents. J. Hazard. Mater. 136, 482—501.

Wastewater Technology Center, 1991. Proposed Evaluation Protocol for Cement-based Solidified Wastes (Canada).

Weng, C.H., Huang, C.P., 1994. Treatment of metal industrial wastewater by fly ash and cement fixation. J. Environ. Eng. 120, 1470—1487.

Wu, X., Tan, X., Yang, S., Wen, T., Guo, H., Wang, X., Xu, A., 2013. Coexistence of adsorption and coagulation processes of both arsenate and NOM from contaminated groundwater by nanocrystallined Mg/Al layered double hydroxides. Water Res. 47, 4159—4168.

Yi, Y., Liska, M., Al-Tabbaa, A., 2013. Properties and microstructure of GGBS-MgO pastes. Adv. Cem. Res. 26, 114—122.

You, Y., You, Y., Zhao, H., Zhao, H., Vance, G.F., Vance, G.F., 2002. Surfactant-enhanced adsorption of organic compounds by layered double hydroxides. Colloids Surf. 205, 161—172.