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Title: Chemical Performance of Stabilised / Solidified Zinc Contaminated Soil

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Abstract: Stabilisation / solidification has been found to be a relatively sustainable and economical method for managing risks associated with contaminated land. The technology has been employed extensively over the last three decades, particularly for the containment of heavy metals. However, since contaminants are not removed, there is a need to validate the long-term effectiveness of the technique. This requires knowledge of the containment mechanisms, the kinetics of contaminant release (equilibrium and disequilibrium conditions), and identification of the reactive surfaces that induce containment. In the present work, cement stabilised zinc contaminated kaolin clay containing 1% humic acid was tested to evaluate chemical performance in the long-term, Time dependent (chemical kinetics) and pH dependent (equilibrium conditions) and equilibrium porewater leaching were evaluated, using LeachXS and geochemical speciation modelling using ORCHESTRA (embedded in LeachXS). Results showed that zinc was effectively contained within the waste form matrix under the prevailing chemical conditions, with immobilisation increasing with hydration. Presence of humic acid increased the availability of zinc at early stage, but this decreased at later stages and was comparable to organic free-matrices

Key words: Stabilisation/solidification, leach assessments, geo-chemical performance, durability

Introduction

Currently, more than half of the global population lives in cities and this will increase to around 60% by 2030 (United Nations Population Fund, 2007). Developed countries have larger urban populations, and as city sizes increase (Pickett *et al.*, 2010); brown-field land will be needed for development. In order to optimise the development of a brown-field site, a risk-based remedial solution will be required to address potential impacts on the environment (Shepherd *et al.*, 2006; Nathanail, 2009; Pavao-Zuckerman, 2008; Lerner and Harris, 2009).

Sustainable urban development requires a wide appreciation of environmental and geology related impacts (Marker, 2009). Embedded within this the concept of resilience further helps to obtain a complete understanding of the risks and vulnerabilities associated with future development decision-making (Manyena, 2006), and should be systematically built into the planning and design process (Bosher *et al.*, 2007). Thus the development (and application) of sustainable and resilient engineering principles encompasses changes in prevailing conditions, and informs risk-based design measures. This is particularly pertinent to treatment of contaminated sites, where a wide variety of methods can be employed depending on the contaminant present.

Stabilisation / Solidification (S/S) have been found, for example, to be particularly suitable for the containment of heavy metal contaminants (Bone *et al.*, 2004, Harbottle *et al.*, 2008), relying on the interaction between cementitious binders and contaminated material, to chemically fix or physical encapsulate toxic materials into more stable forms with desired physical and chemical properties (Connor, 1990). However, since contaminants are not

removed, confidence in the long-term performance (and chemical durability) of the stabilised material is required

This paper presents chemical performance evaluation criteria, of the type required to ensure long-term effectiveness of S/S treatment for heavy metal contaminated soils. Here, cement-stabilised zinc contaminated kaolin clay, containing 1% humic acid, was evaluated, by three periodic assessments over a period of about 10 months (28, 150 and 300 days of hydration). Leaching, augmented by geochemical speciation using LeachXS embedded with ORCHESTRA were used to establish the basis for the approach adopted.

STABILISATION / SOLIDIFICATION

The stabilisation process involves mixing of reagents / binders with contaminated soil to achieve the desired containment physical and chemical properties, and can be undertaken in-situ or ex-situ (Conner, 1990, Bone *et al.*, 2004). An extensive review of scientific literature on the application of S/S for treatment of contaminated soils, solid wastes and sludges have been undertaken by the UK Environment Agency, and presented in Bone *et al.*, (2004). Treatability and pilot studies are required prior to the site application of S/S, to optimise the mix and operational design, determine suitability and applicability for the prevailing conditions. This is often undertaken at 28 days of binder hydration, which for the use of cement binders will have achieved 65% hydration, with an excess of 90% hydration after 1 year (Bone *et al.*, 2004). Portland cement is commonly used as a binder for S/S due to its hydraulicity, which induces strength, reduced permeability and increased durability with time (Conner, 1990). The alkaline environment favours the immobilisation of toxic heavy metals (Conner, 1990, Bone *et al.*, 2004, Chen *et al.*, 2008), and the formation of cementitious minerals, precipitates and complex-products all of which enhance containment. A review of the immobilisation mechanisms for heavy metals during cement S/S is presented in Chen *et al.*, (2008).

To understand the application of S/S, the use of a conceptual study is appropriate, to visualise the binder addition and alteration of the material with binder hydration John, (2011). Figure 1 shows a conceptualisation of the binder application process, and the formation of products that induce containment of contaminants. Figure 2 shows a magnified view of the formed products and the contaminant containment mechanisms within the stabilised material. Note that in Figure 2, sorption on the clay surface is due to the electronegative properties of the clay surface, which sorption into clay is due to cation exchange, replacement or lattice substitution.

Figure 1

Figure 2

Minerals such as kaolinite may be pozzolanic (Bell, 1996) and may be active in immobilisation of contaminants by the formation of complexation products. For zinc (the contaminants of interest in the current study), the presence of aluminium in the crystalline lattice and silicic acid (H_4SiO_4) in the equilibrium solution favours the prevalence of zinc silicates in controlling solubility (McPhail *et al.*, 2003). Also, during binder hydration zinc complexes with calcium to form calcium zincate, which coats the surfaces of calcium silicate hydrate (CSH) gel, which forms during cement hydration (Mollar *et al.*, 1995). The high alkalinity associated with cement hydration also favours formation zinc hydroxides sorbed or incorporated into the interlayer of CSH (Zeigler *et al.*, 2001). However, if pH decreases from high alkaline (above about 12) to around 10.5 (e.g. resulting from environmental degradation), most cementitious minerals become decalcified and portlandite will dissolve releasing about 80% of the available calcium and sulphur (Engelsen *et al.*, 2009, Martens *et al.*, 2010). Degradation in this way would adversely impact on the immobilisation of contaminants bound in a cement-based system.

102

103

104 **Leaching Evaluation and Chemical Characterisation of Stabilised Materials**

105 An integrated assessment framework is required for evaluating leaching from materials, taking
106 into account the intrinsic and extrinsic impacts on the different release controlling constraints
107 (Kosson *et al.*, 2002). The reactive components such as hydrous ferric oxides, clays and
108 organic matter, that influence immobilisation are important (Van der Sloot *et al.*, 2005).
109 However, pH is the main controlling factor for metal partitioning between the solid and
110 aqueous phase, and different surface process occur within the pH domain (Dijkstra *et al.*,
111 2004). pH and organic matter directly influence metal distribution in soils, while Eh (oxidation
112 – reduction potential) indirectly alters distribution, mainly through pH modification (Peng *et al.*,
113 2009). Contaminant availability determines the leaching potential, and this is controlled by
114 its speciation within the material (Van der Sloot and Dijkstra, 2004). Two types of matrices
115 control leaching behaviour: monolithic and granular. Monolithic materials show diffusion
116 dominated leaching, while granular materials show percolation dominated leaching (Van der
117 Sloot and Dijkstra, 2004). Most cementitious matrices are monolithic in nature, and aqueous
118 leaching is controlled by both chemical and physical transport processes (Van der Sloot and
119 Dijkstra, 2004) and influenced by chemical kinetics with reaction rates that do not reach
120 equilibrium (Bone *et al.*, 2004). However, it is also important to obtain information on the
121 porewater chemistry, and incorporate this into the leaching evaluations to give indications of
122 leaching under low liquid to solid ratios. To incorporate environmental influences, it is
123 important to evaluate leaching under the different chemical constraints that induce leaching,
124 which include equilibrium leaching conditions (pH dependent) and disequilibrium (diffusion,
125 dissolution and mass transfer) leaching conditions. This allows evaluation of leaching under
126 appropriate field exposure conditions, after incorporating extrinsic factors such as oxidation,
127 hydrology and mineralogical changes (Van der Sloot *et al.*, 2007).

128

129 Using this leaching evaluation method, a complete chemical characterisation of stabilised
130 matrices can be undertaken as part of treatability / pilot studies. With due consideration of the
131 solubility controlling mineral phases, their chemical interactions, geochemical speciation
132 modelling can be used to inform decision-making, and improve confidence in S/S. Thus, the
133 role of modelling is important in assessing the dominant geochemical process that control
134 porewater chemistry, long-term leaching, and the fate and transport of contaminants from
135 stabilised materials (Bone *et al*, 2004). Figure 3 shows a flow diagram of the S/S evaluation,
136 validation and application process, with breakdown of requirements for chemical
137 characterisation during treatability studies (John, 2011).

138

139 *Figure 3*

140

141 **Scope of Current Work Presented**

142 The immobilisation of zinc within stabilised kaolin clay is used in the development of a tool to
143 evaluate the long-term performance of S/S waste forms. The effectiveness of chemical
144 durability and the effect of advancing hydration on Zn containment are assessed, under the
145 influence of increased organic carbon (as humic acid). The results are compared to zinc
146 contaminated kaolin clay without humic acid (John *et al.*, 2011a).

147

148 **EXPERIMENTAL DESIGN AND EVALUATION CRITERIA**

149 **Materials and Sample Preparation**

150 To undertake chemical characterisation as part of the evaluation method for the assessment of
151 S/S effectiveness and long-term performance, it was necessary to use materials with relatively
152 well define chemical properties. An additional complexity was then introduced to take into
153 account the influences of some soil components, which in the case of this study was humic

acid. The clay used was PolWhite-E kaolin clay, containing >85% alumina and silica (40% aluminium and silicon), with 40% of particles $\leq 2\mu\text{m}$ and <10% of particles $\geq 10\mu\text{m}$. A Portland – composite cement with the least chemical complexity (CEM II Portland Limestone cement) was chosen as the binder. The mineral composition of the kaolin clay and CEM II Portland Limestone cement are shown in Table 1 (John, 2011).

Table 1

To assess the containment of zinc during stabilisation treatment and the implications of organic carbon on containment, it was first important to assess the typical concentrations observed in field contaminated samples. Inherent heterogeneity of soils in the field makes it difficult to establish a baseline of contaminant concentrations, even for contamination from similar processes. Also, the variable composition of the soils themselves presents a unique challenge, with variable mixtures of sand, clay and silts, and variable compositions of organic and inorganic carbon, not least the variable admixture of heavy metal contaminant cocktails. Zinc concentrations can vary from trace or background levels on Greenfield and uncontaminated sites, to concentrations in g/kg (grams/kilogram) for contamination from zinc smelter processes. These soils can also have varying organic contents, which have significant implications for the containment and leachability of zinc. Stephan *et al.* (2008) assessed the speciation of zinc in soils sampled from 66 sites of varying land-use (agricultural, urban, forest and industrial) in Europe and the Americas, and found zinc concentrations between 11 and 3612 mg/kg, with over 80% of concentrations between 100 and 500mg/kg. Perez-Esteban *et al.* (2012) also found zinc concentrations of 146 and 203mg/kg for contaminated clayey silty sands around old copper and blende mines north of Madrid, while Beesley *et al.* (2010) found zinc concentrations of 790 – 930mg/kg in dredged canal sediments (Silty sands containing 6-8% clay) from the Staffordshire canal in the UK. Hale *et al.* (2012) found 657mg/kg available

zinc 2.7% inorganic carbon, 0.6% organic carbon clayey sands from an industrial site in Ontario, Canada, and 34mg/kg concentration in 0.05% inorganic carbon, 3.4% organic carbon clayey sands from an urban soil in Sudbury Ontario. These variable zinc contents from contaminated sites or varying soil compositions highlight the difficulty for replication under laboratory conditions, and the variable soil composition highlights a potential challenge with effectively characterising the soil behaviour during cement treatment. However, it should also be noted that large values for zinc contamination in soils are observable for soils contaminated by zinc smelter operations. Nachtegaal *et al.* (2005) observed a concentration range of 2000 – 18,550mg/kg of zinc from a former zinc smelter site in North East Belgium, with a maximum spike measured at 20,476mg/kg. Volgar *et al.* (2011) also measured concentrations between 2074 and 42,039mg/kg from a zinc smelter process contaminated soil in Slovenia. For the presented study, 500mg/kg was selected as the contaminant concentration utilised, which is acceptable for a range of zinc concentrations in contaminated sites as observed from reported literature. Also, considering the low organic content in kaolin, 1% organic matter (humic acid) was deemed sufficient for assessment.

Detailed description of the laboratory sample preparation process and detailed experimental methodology is presented in John *et al.* (2011b), including the details of the equipment configurations, mixing and packing methods, and quality control. Treatability studies were undertaken to optimise the sample preparation process and improve homogeneity, including the mixing and packing processes, as reported by John (2011). Technical grade humic acid powder was added to the dry kaolin clay to evaluate the influence of soil organic matter on contaminant containment, using 1% (total mix weight) of solid humic acid. The contaminant sorption capacity test (ASTM D4646-03, 2008) was used to determine the maximum amount of zinc that could be sorbed by kaolin. This was determined to be 322mg/kg under the natural chemical condition of kaolin, with some induced acidity by the addition of the zinc as zinc nitrate hexahydrate (John, 2011). Analytical grade zinc nitrate hexahydrate was added at a rate

of 500mg/kg (zinc to total mix weight) to kaolin along with 1% (total mix weight), and mixed at an initial 20% (total weight) water content to consistency (See John *et al.* 2011b). Zinc nitrate hexahydrate was added with the 20% water, while the humic acid was hand mixed in with the dry kaolin prior to addition of water and mixing to consistency in the mixer. The mixture was then placed in sealed plastic bags and stored for 48 hours at 20°C for maturation, to ensure cation exchange and mixture equilibration occurred prior to stabilisation. For the experimental process, 10% (total mix weight) cement was used to stabilise the contaminated clay, and this was added as slurry with 8% water to the pre-mixed and equilibrated contaminated clay with 1% humic acid. The final mix design contained approximately 89% kaolin clay, 1% humic acid, 500mg/kg zinc, stabilised with 10% CEM II Portland Limestone cement, mixed at 28% (final water content) water content (total mix weight). After stabilisation, the mix was packed in 10cm long 10cm diameter polyvinyl chloride (pvc-u) pipes using vertical compression via an air pump (ENERPAC 10,000psi Turbo II) in three equal layers, at a bulk density of 1600kg/m³ [should give dry density – 1250kg/m³]. The pipes were then capped and sealed with silicon sealant to prevent air ingress-and stored at 20°C for the required durations prior to testing.

Leaching and Extraction Tests

To address the equilibrium and disequilibrium release controlling mechanisms, a suitable suite of leaching tests had to be established, to provide information on components releases under the prevailing constraints. Also, to estimate the amount of reactive hydrous ferric oxide (HFO) surfaces, extractions for oxalate (amorphous aluminium), ascorbate (amorphous iron) and Dithionite (crystalline iron) were undertaken, according to Dzombak and Morel (1990). All chemical leaching or extraction tests and chemical parameter measurements were undertaken at a constant temperature of 20±1°C. The primary leachant employed for testing was demineralised water, obtained through reverse osmosis.

232

233 **Time Dependent Leaching**

234 To assess disequilibrium time-dependent leaching, the dynamic monolithic leaching test with
235 periodic leachant renewal CEN/TS 15863 (2008) was employed. The leachant was
236 demineralised water, however, a 9th leachant renewal step was included (at 64 days), to
237 evaluate longer hydration times. Monolithic specimens (10cm long 10cm diameter cylindrical
238 samples) were tested at 8 ± 0.1 L/A (liquid leachant to specific surface area ratio), and to protect
239 the eluate from degradation, the leaching vessels were sealed immediately after pH and
240 conductivity were measured. The monolithic specimens were extruded and cleaned with a soft
241 brush prior to testing, and tests were undertaken along the guidelines of CEN/TS 15863.
242 Typical values for specific surface areas were 500cm^2 for 10 long 10 diameter specimens,
243 which were leached in approximately 8 litres of demineralised water in the leaching vessels,
244 with the leachant replaced after each sampling interval. Samples were completely immersed
245 during leaching, with a minimum liquid displacement of 20mm around the samples during
246 testing in the leaching vessel. Sampling and replacement was undertaken using a peristaltic
247 pump, as the leaching vessels were sealed to prevent excessive air interactions, with provisions
248 made for the insertion of flexible plastic pipes for sample collection and replacement.

249

250 **pH Dependent Leaching**

251 For equilibrium pH dependent leaching assessments, the pH dependent leaching test CEN/TS
252 14429 (2008), with initial addition of acid or base was employed. Samples were crushed to
253 achieve a particle size below 2mm in a porcelain bowl, and demineralised water was used as
254 the primary leachant, with pH adjusted by additions of 2mol nitric acid or 1mol sodium
255 hydroxide. Samples were hand crushed in porcelain bowl to prevent excessive aeration and
256 carbonation by using a crusher. The samples were then passed through a 2mm sieve, and then
257 weighted and air dried at 20°C prior to testing. A pH range of 4 – 12 was required, with a pH

difference of no more than 1.5 pH units between successive samples at relatively large liquid to solid ratios of 20 ± 1 : 1. This liquid to solid ratio is the ratio of leachant to the test specimen, with higher ratios providing a larger volume of leachant relative to the mass of the test specimen. Typically, 10 grams of the solid sample was leached with 200ml of demineralised water and acid or base as required, with the leachant prepared in volumetric flasks using the predetermined amount of acid / base (via titration and equilibration over 24 hours due to the buffering capacity of the specimens) which is added to the primary leachant (demineralised water). Testing was undertaken using an end over end shaker at 10rpm (revolutions per minute), with the leachant added in three steps over two hours. . pH was measured at 4, 44 and 48 hours, and a maximum variation of 0.3 pH units was required between 44 and 48 hours to ensure equilibration had been attained during testing.

Porewater Leaching

Most leaching tests are carried out at relatively high L/S ratios (such as 20:1 employed for the pH dependent leaching tests), and do not give insight into leaching under often low L/S conditions (porewater) encountered in the field (Van der Sloot *et al.*, 2006). For the current study, the up-flow percolation test CEN/TS 14405 (2008) was employed to evaluate leaching, using eluate obtained from the first 3 fractions of the test up to a cumulative L/S ratio of 0.5. Here, 500ml of demineralised water will be passed through 1kg of the test sample. Samples were crushed under controlled conditions to prevent excessive aeration and carbonation, and tested in 32cm long 10 cm diameter cylindrical columns at a flow rate of 48ml/h. Prior to testing, samples were saturated with demineralised water, and allowed to stand for 4 days to reach equilibrium conditions. The first two fractions (0.1 L/S each) were used for validation that equilibration of the samples have been attained, and should not vary by more than 0.5 pH units. If conditions were met, the two fractions were combined to form one sample (cumulative 0.2 L/S fraction) prior to analysis.

284

285 **Hydrous Ferric Oxide (HFO) Extraction**

286 HFO extractions were undertaken along the guidelines prescribed by Dzombak and Morel
287 (1990), using the ascorbate extraction method to determine the amorphous iron content, the
288 dithionite extraction method to determine the crystalline iron content, and the oxalate
289 extraction method to determine the amorphous aluminium content. For modelling purposes,
290 amorphous aluminium is treated similar to amorphous iron, where 1mol amorphous iron \approx
291 1mol amorphous aluminium (Dijkstra *et al.*, 2004), using recommended specific surface areas
292 of 600m²/g for aluminium and 100m²/g for crystalline iron (Meima and Comans, 1998).
293 Results for HFO (iron and amorphous aluminium) used as part of modelling inputs are
294 presented in Table 2. Kaolin dissociates under alkalinity with gibbsite becoming stable through
295 silica loss (Langmuir, 1997), and thus HFO content may change with hydration. However, for
296 the current study, measurements were taken at 150 days, and assumptions of constant HFO
297 content made for consistency.

298

299 *Table 2*

300

301 **Leaching Assessments and Modelling Tools**

302 Leaching assessments were undertaken using the leaching expert system and database
303 LeachXS, embedded with the geochemical speciation modelling tool ORCHESTRA (Van der
304 Sloot *et al.*, 2007). ORCHESTRA uses geochemical information from the extended
305 MINTEQA2 database (US EPA speciation database), models organic carbon interactions using
306 the NICA-Donnan model (Van der Sloot *et al.*, 2005), and models sorption to HFO according
307 to the generalised 2 layer model of Dzombak and Morel (1990). Leaching information from the
308 different tests, material properties, leaching parameters, and extraction information were input
309 into LeachXS, from where leaching evaluations were undertaken. Speciation determinations

(via embedded ORCHESTRA) were then undertaken, and the relevant mineral phases selected based on expected mineralogy of the stabilised matrix under the prevailing conditions prior to modelling. LeachXS – ORCHESTRA combination provides quick data retrieval, automatic input generation for modelling, processing of calculated results and data presentations (Van der Sloot *et al.*, 2005). It allows updating and modification of speciation information, expansion of the thermodynamic database, a constantly expanding repository of speciation and leaching, and is ultimately a holistic platform for undertaking qualitative and quantitative leach assessments.

LEACHING ASSESSMENTS AND GEOCHEMICAL MODELLING

Eluates from the different chemical leaching tests and extractions were undertaken using an ICP-OES (inductively couple plasma – optical emissions spectroscopy) for cation analyses, and using a Shimatzu high sensitivity organic carbon analyser for dissolved organic carbon (DOC) measurements. Table 3 shows the detection limit of the ICP-OES equipment for the elements presented, and the measure of total organic carbon used for modelling was the volume added to make 1% humic acid considering the low organic carbon of the utilised kaolin clay. Leaching evaluations were then undertaken using LeachXS for the stabilised zinc contaminated kaolin clay with 1% humic acid (denoted by EOHZ) to determine the effectiveness of treatment, chemical durability and changes in these properties with hydration. To evaluate the implications of the increased organic content on the contained zinc, findings and results were compared to those for a comparable matrix without increased organic content (John *et al.*, 2011a). Results required for the comparison of cumulative release and component availability without the additives (denoted by EOZ) are included for the different hydration durations (28, 150 and 300 days).

Table 3

Chemical Durability

To evaluate chemical durability, two key factors were considered: the stability of the contaminants under prevailing chemical conditions; and the stability of the structural cations for the kaolin clay (aluminium and silicon). Table 4 shows the time dependent cumulative release of elements (Al, Si and Zn) from monolithic test specimens, including calcium, for comparison with the stabilised mixture without humic acid, at the different hydration durations. These results are presented in grams per square meter of the measured surface area, for leaching due to chemical kinetics with time, via diffusion, dissolution and surface wash off from the stabilised materials natural chemical conditions (CEN/TS 15863, 2008). It is important to understand that the releases of zinc were in trace amounts, where 0.004g/m² observed for EOZ at 28 and 150 days represent the cumulative measure for the zinc detection limits of the equipment, which was used as the minimum value rather than zero. Zinc release was not observed under alkaline conditions during pH dependent leaching assessments, at the different periods of hydration (Figure 4a). This confirms the observations from the time dependent leaching assessments from monolith assessments, at the stabilised materials natural chemical conditions. However, theoretical solubility of zinc as a hydroxide should yield an amphoteric (higher leachability at both high and low pH, and lower leachability under neutral conditions) leaching trend, which was not observed for the stabilised matrices. This was likely due to speciation of the mineral precipitates, a trend also observed from leaching data in Hale *et al.* (2012), for leaching from 15% cement stabilised contaminated soils. Figure 4b shows the evolution of pH during time dependent leaching for monolithic stabilised zinc contaminated kaolin clay with 1% humic acid at the different durations of hydration. This test was undertaken on monolithic specimens at the stabilised materials natural chemical conditions using demineralised water, and the presented pH shows the evolutions in measured pH for samples at different sampling durations. The data presented in Figure 4a are in mg/kg, based on

measured concentrations in analysed eluates, and graphs are presented in log scale to capture the range of concentrations and time (Figure 4b) presented.

From the evaluation of porewater leachability at low L/S ratios (CEN/TS 14405, 2008), it was observed that zinc was not readily mobilised from the stabilised matrix under the prevailing chemical conditions (all measurements below detection limit), while aluminium and silicon release were minimal. These results are thus not presented within this report, but were included during speciation modelling to determine the relevant solubility controlling mineral phases.

Table 4

Figure 4

Considering kaolin dissociates in alkaline conditions, it was important to evaluate durability in view of the structural components for the kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$. Time dependent cumulative releases indicate increasing aluminium availability with increasing [over a period up to 300 days) hydration, further suggesting an increasing of dissociation during this process. Silicon and calcium availability, however, decreased with hydration (Table 4) (over a period up to 300 days) due to silicic acid (H_4SiO_4)-calcium complexes forming stable cementitious minerals. Table 5 shows the maximum availability of the selected components during pH dependent leaching, and indicates that less than 1% of the total structural cations (85% alumina and silica or 40% aluminium and silicon present in kaolin clay) are available for release from the stabilised material. This indicates that the availability of dissolution product decreases at increased hydration durations, which suggests that even though dissociation is taking place, the products are used up for formation of stable mineral precipitates. This is consistent with observation on stabilised clay soils made by Bell (1996), McKinley *et al.* (2001) and Bone *et al.* (2004). Figure 5 shows the time dependent leaching and cumulative releases of silicon and

aluminium at the different hydration durations. The pH dependent leaching trends for aluminium and silicon are presented in Figure 6 at the different hydration times. These results are presented to show concentrations in the analysed eluates, and are also presented in log scale to capture the range of time (Figure 5) and concentrations (Figure 6) covered. The change in the leachability of silicon and aluminium (Figure 5A and 5C) drop sharply at 19 days due to the short leachant renewal period. The pH dependent trends (Figure 6) were not significantly different at the range of time periods examined, but the solubility of aluminium (under neutral conditions; Figure 6A) is influenced by the presence of gibbsite resulting from kaolin dissociation. Modelling indicated that the solubility of aluminium was controlled by kaolinite, montmorillonite, gibbsite, hydrated calcium aluminosilicates, hydrated calcium aluminates, ettringite and organic matter; whereas silicon was controlled by kaolinite, jennite, calcium silicate hydrate, hydrated calcium aluminates, hydrous ferric oxides and zinc silicates.

Table 5

Figure 5

Figure 6

Zinc Containment

Table 4 shows that zinc was not leached over time under the material's natural conditions. Table 5 shows that the availability of zinc decreases with increasing period of hydration. Kaolin clay with additives (EOHZ), had increased zinc availability at early age, but this decreased with time up to 300 days, when results were comparable to the control mixture. Also, at 28 days of hydration almost all introduced zinc is available for leaching (0.5grams/kg). Zinc silicates are likely to prevail with presence of silicic acid in the pore solution and aluminium in the crystalline lattice (McPhail *et al.*, 2003), and the presence of increased organic containment retards cement hydration (Bone *et al.*, 2004). This retardation is likely due

to hydration when more stable products form through decreased kaolin dissociation and complexation of zinc with organic carbon, which are responsible for the increased availability in the humic acid matrices. As hydration progresses past this retardation, more silicic acid becomes available in the pore solution for complexation with zinc, and more zinc is complexed with the formed cementitious products, which induced increased containment as seen at the advanced hydration period (Table 5).

Zinc may be incorporated by the kaolin clay to form a range of potential species. Fraipontite - $(\text{Zn, Al})_3(\text{Al, Si})_2\text{O}_5(\text{OH})_4$, complexed with calcium to form calcium zincate, or precipitated as insoluble zinc silicates. Predictions of speciation also suggest a range of zinc silicates can be formed: metastable zinc silicate (ZnSiO_3) complexes with magnesium $(\text{Zn, Mg})\text{Si}_2\text{O}_6$, as Willemite - Zn_2SiO_4 , or as hydrated hercynite $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$. Under the prevailing conditions, it was expected that all these mineral formations are possible, but some like hercynite and fraipontite lack sufficient thermodynamic information for use in modelling (McPhail *et al.*, 2003). These phases were not available for selection during speciation determinations, and for consistency ZnSiO_3 was used to represent all zinc silicates. The use of ZnSiO_3 was also seen in similar modelling work by Comans *et al* (1993) and Meima and Comans (1999), and in both cases amphoteric leaching was observed for zinc releases. However, this was not observed during the current study (Figure 4A), but was comparable to observations of zinc leaching in Hale *et al.* (2012). Figure 7 shows the geochemical speciation modelling predicted and measured releases for zinc, and the predicted solubility controlling mineral phases at the different hydration durations for the stabilised zinc contaminated kaolin clay with 1% humic acid.

Figure 7

These results show predictions for amphoteric leaching, but the measured trends consistently show that zinc was insoluble. Considering the reduced silica solubility observed for the matrix under alkaline conditions (Figure 6B), it is likely that zinc is complexed as an insoluble silicate, such as hercynite, for which thermodynamic information is not available.

The predictions (Figures 7B, 7D and 7F) show that zinc solubility is controlled by zinc silicates, franklinite, calcium zincate, particulate organic matter, and to a lesser degree HFO. By way of interest, Franklinite is a mineral found in granitic rocks from which kaolin clays are weathered.

Figure 8 shows the pH dependent releases of DOC with increasing hydration, which will be dependent on the properties of the utilised humic acid. The results are presented in g/kg, converted to show the releases from the mass of sample, rather than the release into the eluates. The results show that DOC has lower solubility under both alkaline and acidic conditions, with the higher solubility under neutral conditions. However, while DOC releases were elevated under neutral conditions, this did not modify the zinc leachability trend (Figure 4A).

Figure 8

The approach presented in this paper demonstrates how longer term stability of S/S has been evaluated for a zinc contaminated kaolin soil, treated using cement. This work demonstrates the potential for such analysis to be extended for all S/S used in the treatment of soil containing any heavy metal contamination. Thus to fully understand and therefore design S/S for the longer term, knowledge of the release controlling mechanisms, mineralogy, field exposure conditions, and key extrinsic parameters, such as hydrological, redox and, weathering conditions are required. This is achieved through leaching assessments augmented by geochemical speciation modelling a complete assessment can be made.

465

466 **SUMMARY AND CONCLUSION**

467 An evaluation of zinc in Portland cement-bound kaolin shows that it is effectively
468 immobilised, with the potential solubility controlling phases being zinc silicate, franklinite,
469 calcium zincate, organic carbon, and to a lesser degree HFO. The expected amphoteric
470 leaching of zinc was not observed and may be due to the complexation of zinc as insoluble
471 silicates. The presence of humic acid increased the initial availability of zinc.

472

473 The stabilised material was observed to be durable as less than 1% of structural cations (Al and
474 Si) were available after 300 days, with silica decreasing with period of hydration. Although
475 kaolin dissociated with time, zinc containment was maintained via the formation of zinc
476 silicates.

477

478 The approach adopted in this paper for the chemical characterisation of cement-treated kaolin
479 mixtures can be used to inform a performance based S/S design approach, and is reliant on
480 knowledge of the release controlling mechanisms, mineralogy, field exposure conditions, and
481 key extrinsic parameters, such as hydrological, redox and, weathering conditions. However, it
482 should be noted that gaps still exists in the thermodynamic database, and this may impede
483 performance-based S/S remedial designs.

484

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488

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Table 1: Mineral compositions of kaolin clay (PolWhite-E) and CEM II Portland limestone cement (John, 2011)

Kaolin Clay		CEM II Portland Limestone Cement	
Mineral	Presence (%)	Mineral	Concentration (%)
Kaolin	74-80	SiO ₂ – Silicon Oxide	16.9
Feldspar	5-12	Al ₂ O ₃ – Aluminium Oxide	4.3
Quartz	1-2	Fe ₂ O ₃ – Ferric Oxide	2.9
Mica	5-15	CaO – Calcium Oxide	61.9
Montmorillonite	2-3	MgO – Magnesium Oxide	1.0
		SO ₃ - Sulphate	2.7
		Na ₂ O – Sodium Oxide	0.66
		LOI – Loss on Ignition	9.2
		Free CaO	2.1

Table 2: HFO content for stabilised zinc contaminated kaolin clay, and stabilised zinc contaminated kaolin clay with 1% humic acid. Here, EOZ represent zinc contaminated kaolin clay, and EOHZ represents zinc contaminated kaolin clay with 1% humic acid.

Sample	Extraction	Aluminium	Total Iron	Crystalline Iron	HFO (kg/kg)
	Ascorbate		(mol/kg)		
			0.00336		2.99E-04
EOZ	Dithionite		0.00416	0.00080	1.19E-05
	Oxalate	0.02036			1.81E-03
				Total HFO	2.12E-03
	Ascorbate		0.00254		2.26E-04
EOHZ	Dithionite		0.00487	0.00234	3.47E-05
	Oxalate	0.00373			3.32E-04
				Total HFO	5.92E-04

Table 3: Detection limits for presented elements, for utilised ICP-OES equipment

Element	Detection Limit (µg/l)
Zinc	0.070
Aluminium	0.040
Silicon	0.900

Table 5: Availabilities of selected components during pH dependent leaching from the stabilised zinc contaminated kaolin clay without additives (EOZ) and the stabilised zinc contaminated kaolin clay (EOHZ) at the different hydration durations

Zinc Samples Availabilities (g/Kg)					
Sample	pH	Al	Si	Ca	Zn
EOZ 28days	3.76	1.92	2.11	22.48	0.48
EOZ 150days	4.10	0.46	1.09	21.40	0.26
EOZ 300days	3.82	1.09	1.14	22.02	0.20
EOHZ 28days	4.03	0.66	1.77	21.25	0.51
EOHZ 150days	4.26	0.38	1.45	20.24	0.43
EOHZ 300days	4.00	0.45	1.07	19.96	0.23

Table 4: Cumulative releases of components during time dependent leaching from stabilised zinc contaminated kaolin clay (EOZ), and stabilised zinc contaminated kaolin clay with 1% humic acid (EOHZ) at the different hydration durations.

Zinc Samples Cumulative Releases (g/m ²)				
Sample	Al	Si	Ca	Zn
EOZ 28days	3.72	3.91	142.70	0.0004
EOZ 150days	5.33	3.63	61.13	0.0004
EOZ 300days	7.36	3.53	64.63	0.0010
EOHZ 28days	2.29	4.78	185.14	0.0060
EOHZ 150days	4.24	3.78	134.65	0.0009
EOHZ 300days	6.21	3.72	94.05	0.0030

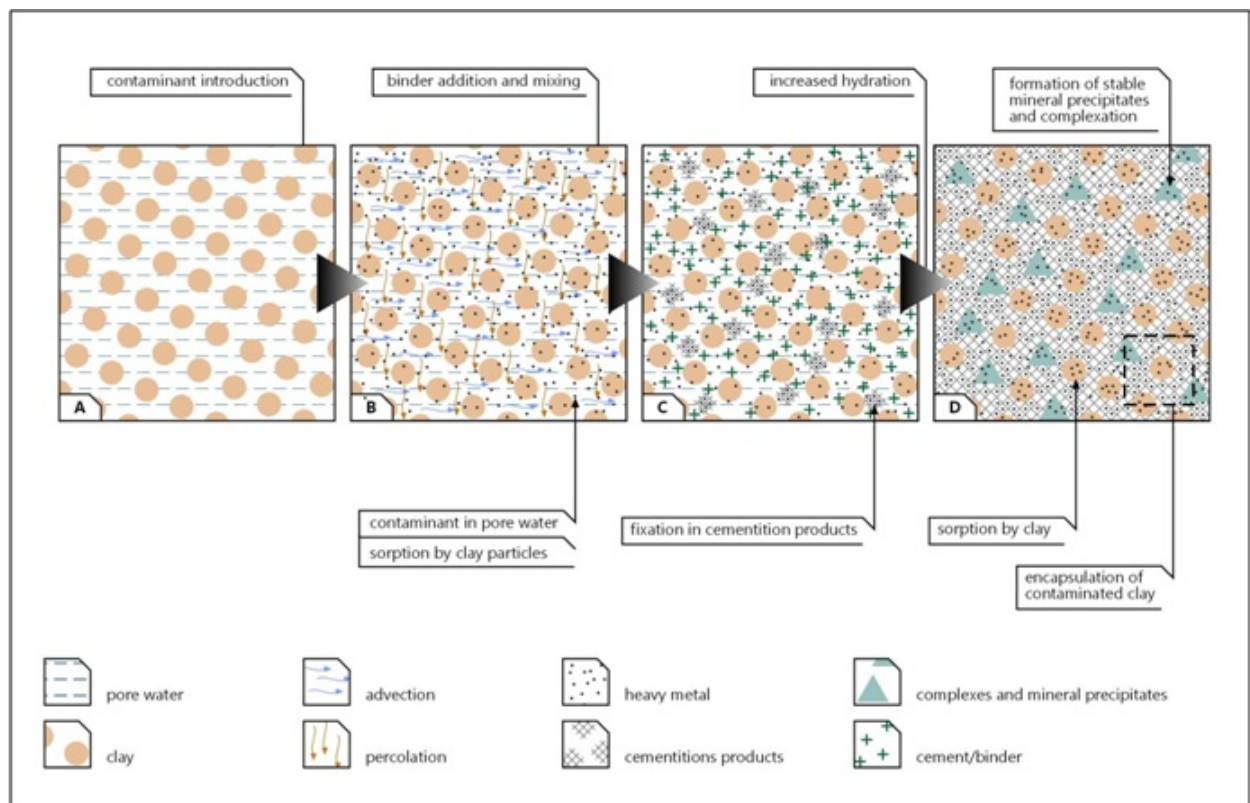


Figure 1: Conceptualisation of binder application process and formations of containment products with increasing hydration (John, 2011)

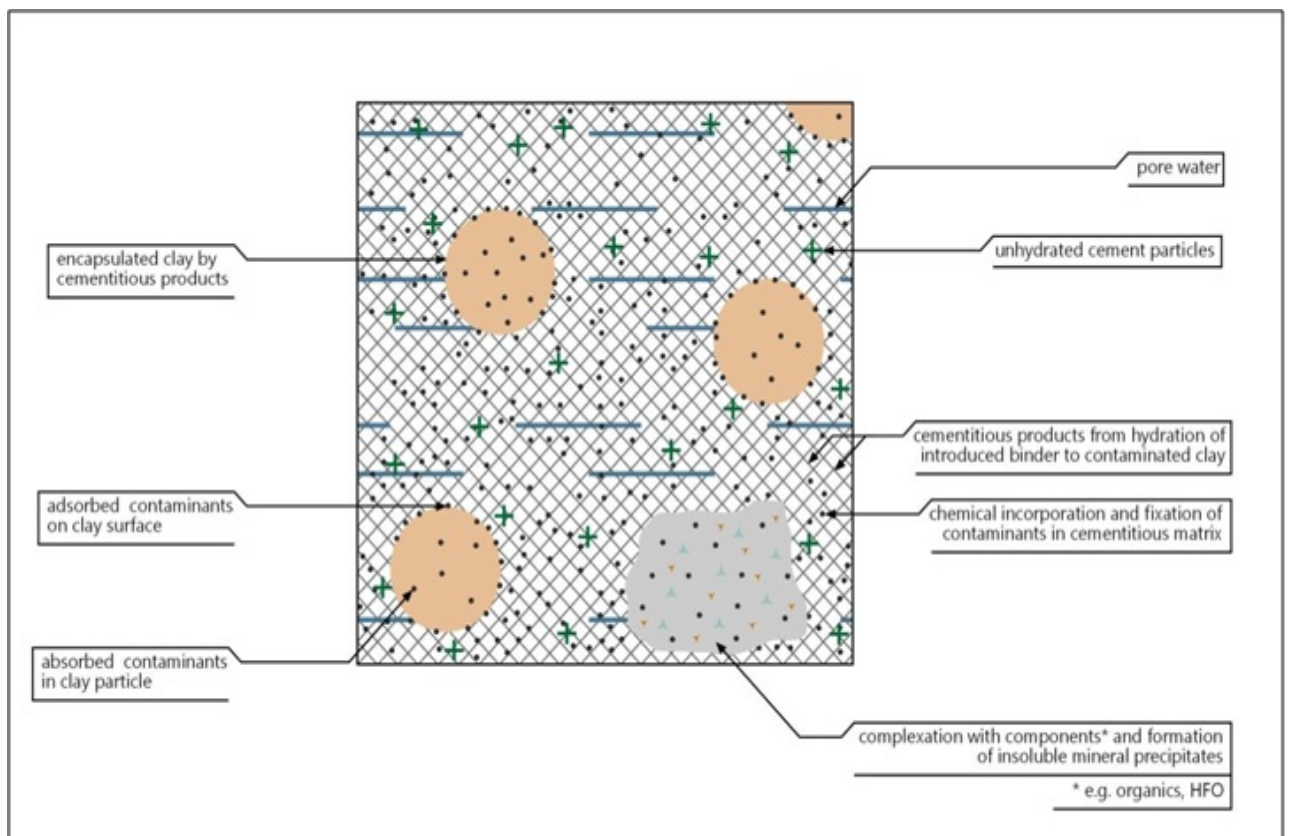


Figure 2: Contaminant containment mechanisms within the stabilised material (John, 2011)

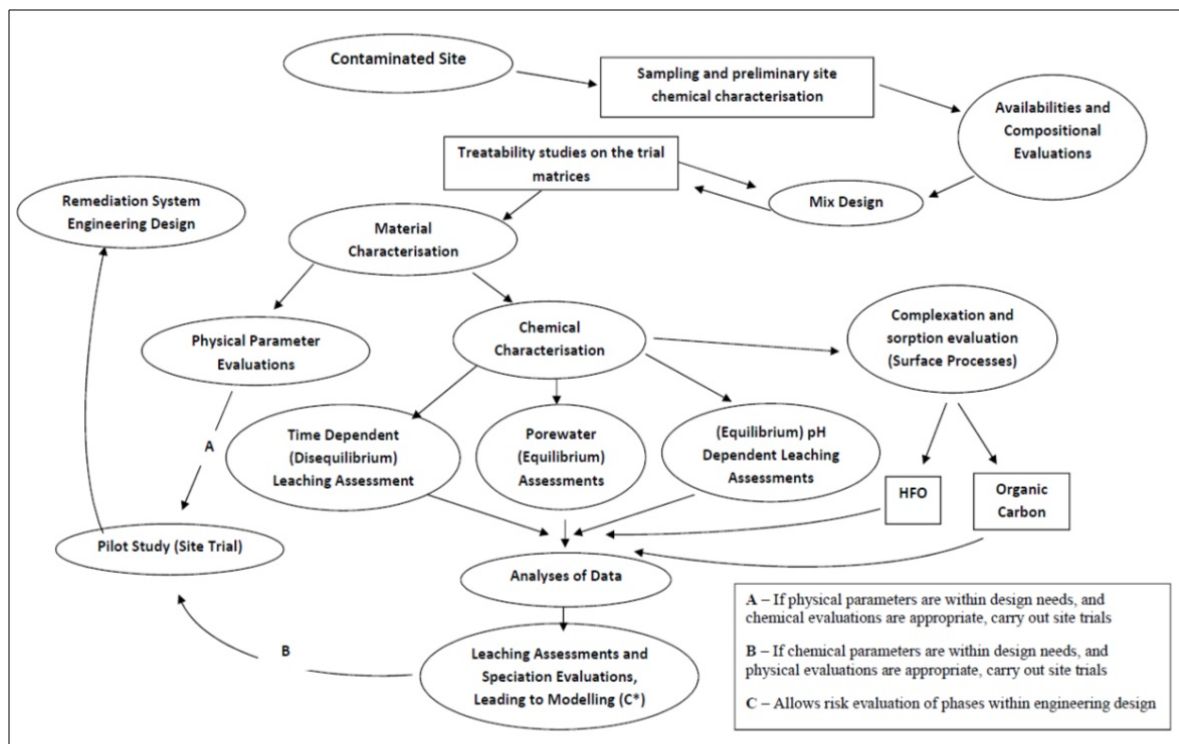


Figure 3: Requirements for material characterisation and evaluation of effectiveness during S/S design, highlighting the chemical characterisation processes (John, 2011)

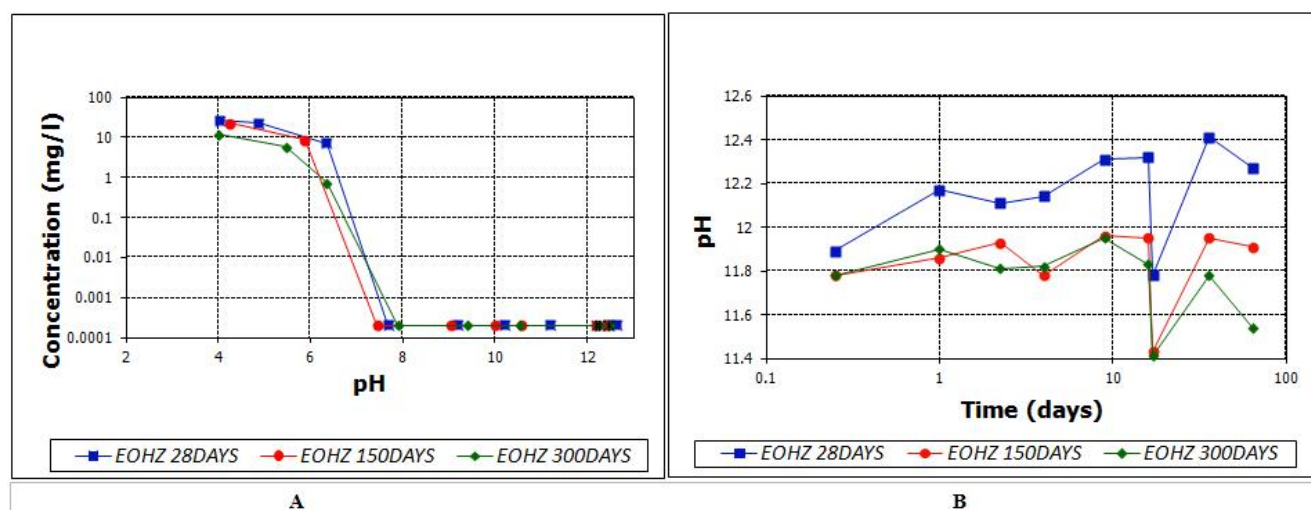


Figure 4: (A) pH dependent leaching of zinc from stabilised zinc contaminated kaolin clay with 1% humic acid. (B) pH evolution during evaluations of time dependent leaching for stabilised zinc contaminated kaolin clay with 1% humic acid.

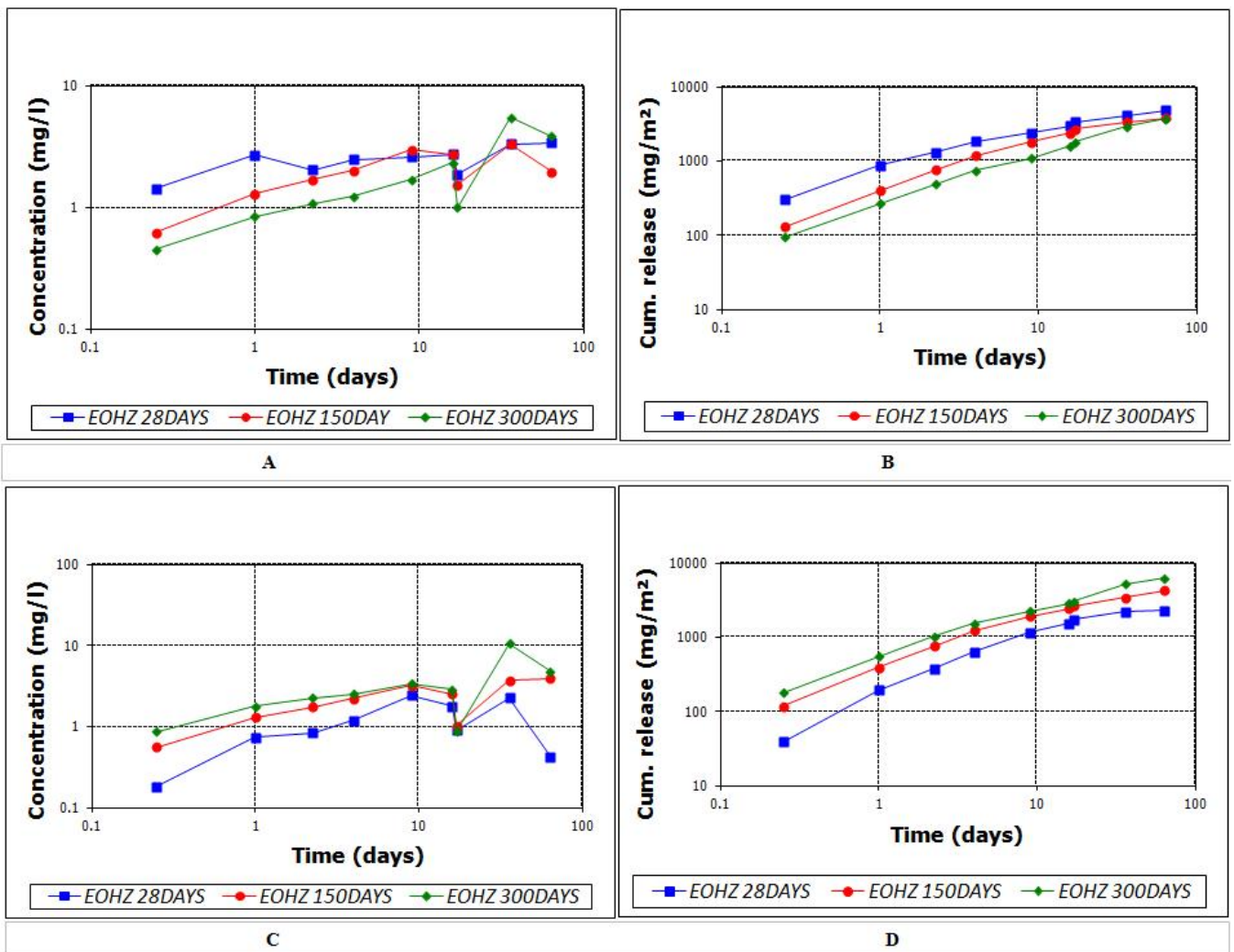


Figure 5: (A) Releases of silicon during time dependent leaching evaluations for stabilised zinc contaminated kaolin clay with 1% humic acid (EOHZ). (B) Cumulative release of silicon during time dependent leaching evaluations for EOHZ. (C) Releases of aluminium during time dependent leaching evaluations for EOHZ. (D) Cumulative release of aluminium during time dependent leaching evaluations for EOHZ.

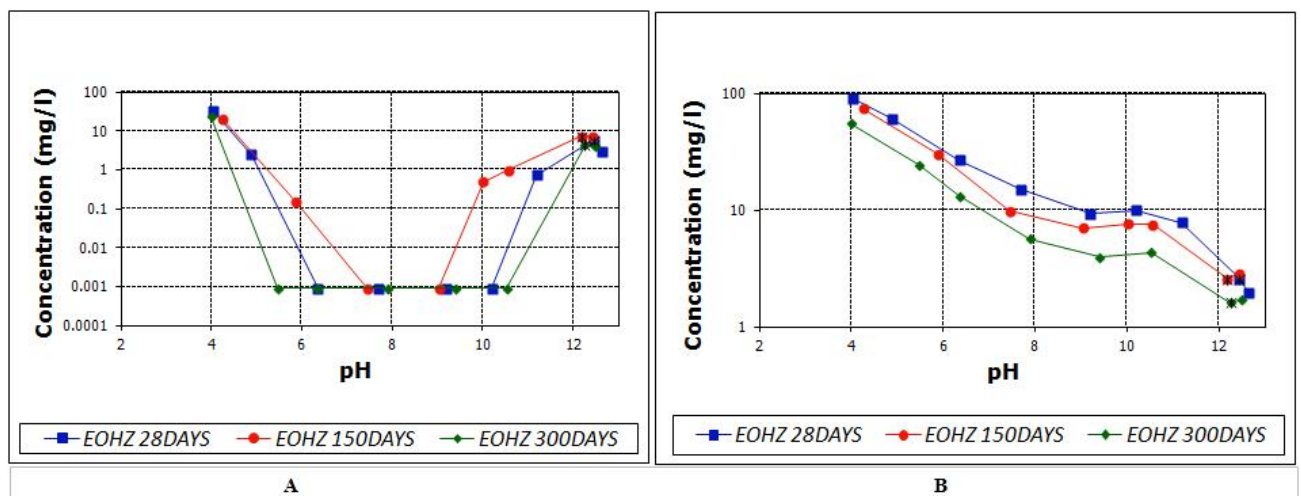


Figure 6: (A) pH dependent leaching of aluminium from stabilised zinc contaminated kaolin clay with 1% humic acid at the different hydration durations. (B) pH dependent leaching of silicon from stabilised zinc contaminated kaolin clay with 1% humic acid at the different hydration durations.

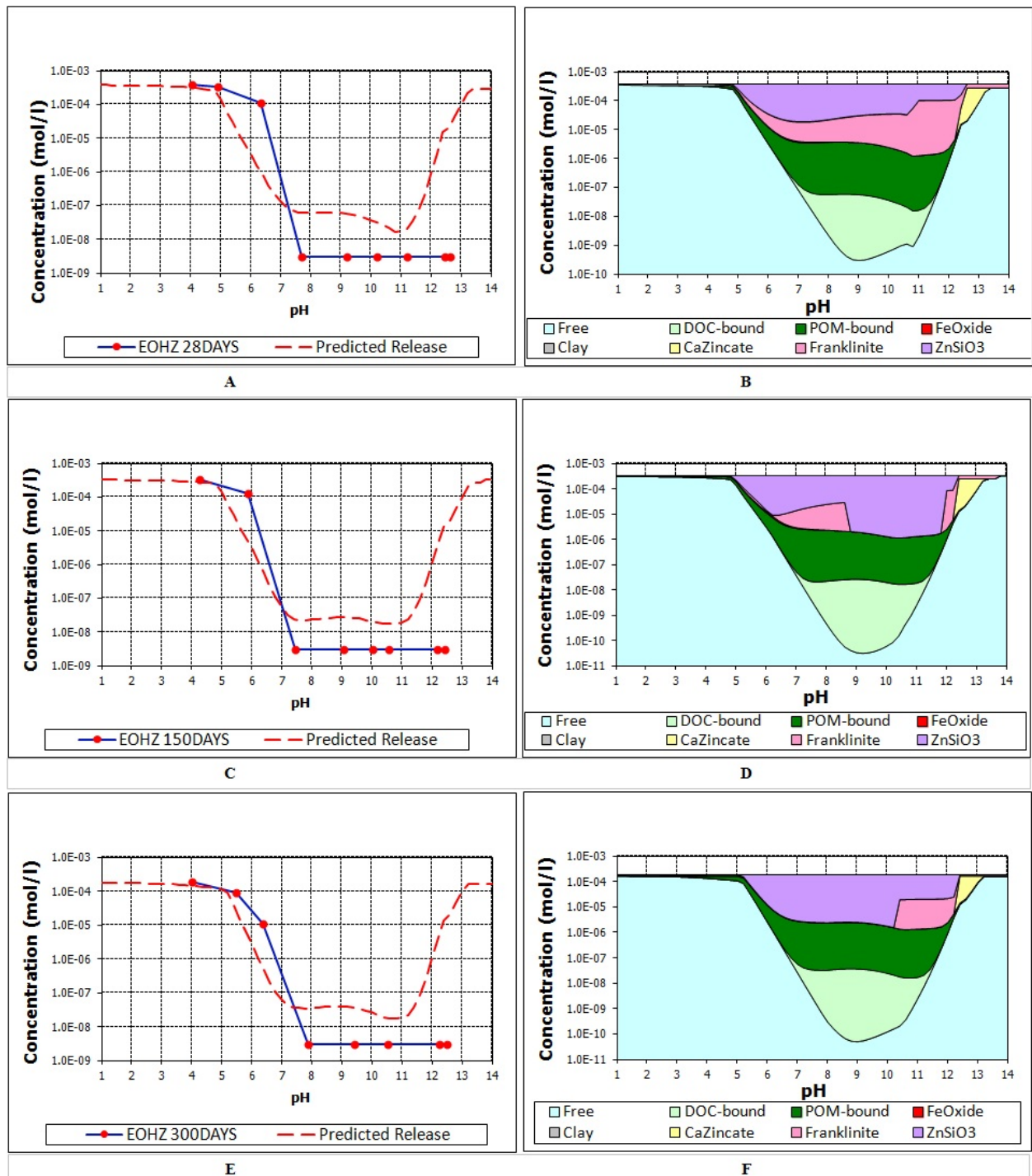


Figure 7: (A) Measured and predicted leaching of zinc leaching at 28 days hydration. (B) Predicted solubility controlling mineral phases for zinc at 28 days hydration. (C) Measured and predicted leaching of zinc leaching at 150 days hydration. (D) Predicted solubility controlling mineral phases for zinc at 150 days hydration. (E) Measured and predicted leaching of zinc leaching at 300 days hydration. (F) Predicted solubility controlling mineral phases for zinc at 300 days hydration.

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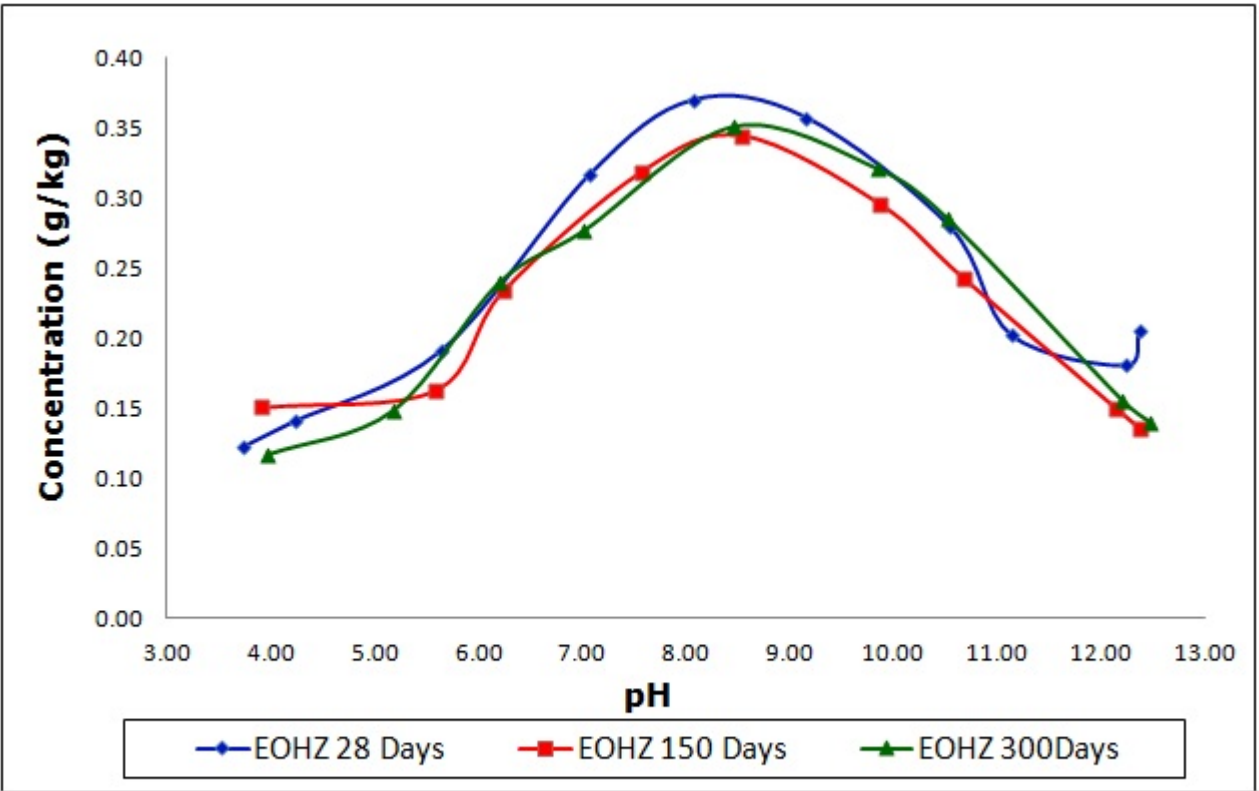


Figure 8: pH dependent releases of DOC from the stabilised zinc contaminated kaolin clay at the different hydration durations.

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