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Chemical performance of stabilized/solidified zinc-contaminated soil

John, Unyime; Jefferson, Ian; Boardman, David; Ghataora, Gurmel; Hills, Colin

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1 **Title**: Chemical Performance of Stabilised / Solidified Zinc Contaminated Soil

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3 **Authors**: U. E. John[1], I. Jefferson[2*], D. I. Boardman[3], G. S. Ghataora[2], and C. D. Hills[4]

4 1: School of Civil Engineering, University of Birmingham, UK

5 2: Senior Lecturer, School of Civil Engineering, University of Birmingham, UK

6 3: Senior Research Fellow, School of Civil Engineering, University of Birmingham, UK

7 4: Reader – School of Science, University of Greenwich, United Kingdom

8 * Corresponding Author (e-mail: i.jefferson@bham.ac.uk)

9

10 **Abstract**: Stabilisation / solidification has been found to be a relatively sustainable and

11 economical method for managing risks associated with contaminated land. The technology has

12 been employed extensively over the last three decades, particularly for the containment of

13 heavy metals. However, since contaminants are not removed, there is a need to validate the

14 long-term effectiveness of the technique. This requires knowledge of the containment

15 mechanisms, the kinetics of contaminant release (equilibrium and disequilibrium conditions),

16 and identification of the reactive surfaces that induce containment. In the present work, cement

17 stabilised zinc contaminated kaolin clay containing 1% humic acid was tested to evaluate

18 chemical performance in the long-term, Time dependent (chemical kinetics) and pH dependent

19 (equilibrium conditions) and equilibrium porewater leaching were evaluated, using LeachXS

20 and geochemical speciation modelling using ORCHESTRA (embedded in LeachXS). Results

21 showed that zinc was effectively contained within the waste form matrix under the prevailing

22 chemical conditions, with immobilisation increasing with hydration. Presence of humic acid

23 increased the availability of zinc at early stage, but this decreased at later stages and was

24 comparable to organic free-matrices

25

28

Introduction

30   Currently, more than half of the global population lives in cities and this will increase to

31   around 60% by 2030 (United Nations Population Fund, 2007). Developed countries have larger

32   urban populations, and as city sizes increase (Pickett *et al.*, 2010); brown-field land will be

33   needed for development. In order to optimise the development of a brown-field site, a risk-

34   based remedial solution will be required to address potential impacts on the environment

35   (Shepherd *et al.,* 2006; Nathanail, 2009; Pavao-Zuckerman, 2008; Lerner and Harris, 2009).

36

37   Sustainable urban development requires a wide appreciation of environmental and geology

38   related impacts (Marker, 2009). Embedded within this the concept of resilience further helps

39   to obtain a complete understanding of the risks and vulnerabilities associated with future

40   development decision-making (Manyena, 2006), and should be systematically built into the

41   planning and design process (Bosher *et al.,* 2007). Thus the development (and application) of

42   sustainable and resilient engineering principles encompasses changes in prevailing conditions,

43   and informs risk-based design measures. This is particularly pertinent to treatment of

44   contaminated sites, where a wide variety of methods can be employed depending on the

45   contaminant present.

46   Stabilisation / Solidification (S/S) have been found, for example, to be particularly suitable for

47   the containment of heavy metal contaminants (Bone *et al.,* 2004, Harbottle *et al.,* 2008),

48   relying on the interaction between cementitious binders and contaminated material, to

49   chemically fix or physical encapsulate toxic materials into more stable forms with desired

50   physical and chemical properties (Connor, 1990). However, since contaminants are not

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

52 material is required

53 This paper presents chemical performance evaluation criteria, of the type required to ensure

54 long-term effectiveness of S/S treatment for heavy metal contaminated soils. Here, cement-

55 stabilised zinc contaminated kaolin clay, containing 1% humic acid, was evaluated, by three

56 periodic assessments over a period of about 10 months (28, 150 and 300 days of hydration).

57 Leaching, augmented by geochemical speciation using LeachXS embedded with

58 ORCHESTRA were used to establish the basis for the approach adopted.

59

60 **STABILISATION / SOLIDIFICATION**

61 The stabilisation process involves mixing of reagents / binders with contaminated soil to

62 achieve the desired containment physical and chemical properties, and can be under taken in-

63 situ or ex-situ (Conner, 1990, Bone *et al.,* 2004). An extensive review of scientific literature on

64 the application of S/S for treatment of contaminated soils, solid wastes and sludges have been

65 undertaken by the UK Environment Agency, and presented in Bone *et al.,* (2004). Treatability

66 and pilot studies are required prior to the site application of S/S, to optimise the mix and

67 operational design, determine suitability and applicability for the prevailing conditions. This is

68 often undertaken at 28 days of binder hydration, which for the use of cement binders will have

69 achieved 65% hydration, with an excess of 90% hydration after 1 year (Bone *et al.,* 2004).

70 Portland cement is commonly used as a binder for S/S due to its hydraulicity, which induces

71 strength,-reduced permeability and increased durability with time (Conner, 1990). The alkaline

72 environment favours the immobilisation of toxic heavy metals (Conner, 1990, Bone *et al.,*

73 2004, Chen *et al.*, 2008), and the formation of cementitious minerals, precipitates and

74 complex-products all of which enhance containment. A review of the immobilisation

75 mechanisms for heavy metals during cement S/S is presented in Chen *et al.,* (2008).

76 To understand the application of S/S, the use of a conceptual study is appropriate, to visualise

77 the binder addition and alteration of the material with binder hydration John, (2011). Figure 1

78 shows a conceptualisation of the binder application process, and the formation of products that

79 induce containment of contaminants. Figure 2 shows a magnified view of the formed products

80 and the contaminant containment mechanisms within the stabilised material. Note that in

81 Figure 2, sorption on the clay surface is due to the electronegative properties of the clay

82 surface, which sorption into clay is due to cation exchange, replacement or lattice substitution.

83

84 *Figure 1*

85 *Figure 2*

86

87 Minerals such as kaolinite may be pozzolanic (Bell, 1996) and may be active in immobilisation

88 of contaminants by the formation of complexation products. For zinc (the contaminants of

89 interest in the current study), the presence of aluminium in the crystalline lattice and silicic

90 acid (H_4SiO_4) in the equilibrium solution favours the prevalence of zinc silicates in controlling

91 solubility (McPhail *et al.*, 2003). Also, during binder hydration zinc complexes with calcium to

92 form calcium zincate, which coats the surfaces of calcium silicate hydrate (CSH) gel, which

93 forms during cement hydration (Mollar *et al.*, 1995). The high alkalinity associated with

94 cement hydration also favours formation zinc hydroxides sorbed or incorporated into the

95 interlayer of CSH (Zeigler *et al.*, 2001). However, if pH decreases from high alkaline (above

96 about 12) to around 10.5 (e.g. resulting from environmental degradation), most cementitious

97 minerals become decalcified and portlandite will dissolve releasing about 80% of the available

98 calcium and sulphur (Engelsen *et al.,* 2009, Martens *et al.*, 2010). Degradation in this way

99 would adversely impact on the immobilisation of contaminants bound in a cement-based

100 system.

101

102

103

Leaching Evaluation and Chemical Characterisation of Stabilised Materials

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

154 acid. The clay used was PolWhite-E kaolin clay, containing >85% alumina and silica (40%

155 aluminium and silicon), with 40% of particles ≤2μm and <10% of particles ≥10μm. A Portland

156 – composite cement with the least chemical complexity (CEM II Portland Limestone cement)

157 was chosen as the binder. The mineral composition of the kaolin clay and CEM II Portland

158 Limestone cement are shown in Table 1 (John, 2011).

159

160 *Table 1*

161

162 To assess the containment of zinc during stabilisation treatment and the implications of organic

163 carbon on containment, it was first important to assess the typical concentrations observed in

164 field contaminated samples. Inherent heterogeneity of soils in the field makes it difficult to

165 establish a baseline of contaminant concentrations, even for contamination from similar

166 processes. Also, the variable composition of the soils themselves presents a unique challenge,

167 with variable mixtures of sand, clay and silts, and variable compositions of organic and

168 inorganic carbon, not least the variable admixture of heavy metal contaminant cocktails. Zinc

169 concentrations can vary from trace or background levels on Greenfield and uncontaminated

170 sites, to concentrations in g/kg (grams/kilogram) for contamination from zinc smelter

171 processes. These soils can also have varying organic contents, which have significant

172 implications for the containment and leachability of zinc. Stephan *et al*. (2008) assessed the

173 speciation of zinc in soils sampled from 66 sites of varying land-use (agricultural, urban, forest

174 and industrial) in Europe and the Americas, and found zinc concentrations between 11 and

175 3612 mg/kg, with over 80% of concentrations between 100 and 500mg/kg. Perez-Esteban *et al*.

176 (2012) also found zinc concentrations of 146 and 203mg/kg for contaminated clayey silty

177 sands around old copper and blende mines north of Madrid, while Beesley *et al*. (2010) found

178 zinc concentrations of 790 – 930mg/kg in dredged canal sediments (Silty sands containing 6-

179 8% clay) from the Staffordshire canal in the UK. Hale *et al*. (2012) found 657mg/kg available

180 zinc 2.7% inorganic carbon, 0.6% organic carbon clayey sands from an industrial site in

181 Ontario, Canada, and 34mg/kg concentration in 0.05% inorganic carbon, 3.4% organic carbon

182 clayey sands from an urban soil in Sudbury Ontario. These variable zinc contents from

183 contaminated sites or varying soil compositions highlight the difficulty for replication under

184 laboratory conditions, and the variable soil composition highlights a potential challenge with

185 effectively characterising the soil behaviour during cement treatment. However, it should also

186 be noted that large values for zinc contamination in soils are observable for soils contaminated

187 by zinc smelter operations. Nachtegaal *et al*. (2005) observed a concentration rang of 2000 –

188 18,550mg/kg of zinc from a former zinc smelter site in North East Belgium, with a maximum

189 spike measured at 20,476mg/kg. Volgar *et al.* (2011) also measured concentrations between

190 2074 and 42,039mg/kg from a zinc smelter process contaminated soil in Slovenia. For the

191 presented study, 500mg/kg was selected as the contaminant concentration utilised, which is

192 acceptable for a range of zinc concentrations in contaminated sites as observed from reported

193 literature. Also, considering the low organic content in kaolin, 1% organic matter (humic acid)

194 was deemed sufficient for assessment.

195 Detailed description of the laboratory sample preparation process and detailed experimental

196 methodology in presented in John *et al*. (2011b), including the details of the equipment

197 configurations, mixing and packing methods, and quality control. Treatability studies were

198 undertaken to optimise the sample preparation process and improve homogeneity, including

199 the mixing and packing processes, as reported by John (2011). Technical grade humic acid

200 powder was added to the dry kaolin clay to evaluate the influence of soil organic matter on

201 contaminant containment, using 1% (total mix weight) of solid humic acid. The contaminant

202 sorption capacity test (ASTM D4646-03, 2008) was used to determine the maximum amount

203 of zinc that could be sorbed by kaolin. This was determined to be 322mg/kg under the natural

204 chemical condition of kaolin, with some induced acidity by the addition of the zinc as zinc

205 nitrate hexahydrate (John, 2011). Analytical grade zinc nitrate hexahydrate was added at a rate

206 of 500mg/kg (zinc to total mix weight) to kaolin along with 1% (total mix weight), and mixed

207 at an initial 20% (total weight) water content to consistency (See John *et al.* 2011b). Zinc

208 nitrate hexahydrate was added with the 20% water, while the humic acid was hand mixed in

209 with the dry kaolin prior to addition of water and mixing to consistency in the mixer. The

210 mixture was then placed in sealed plastic bags and stored for 48 hours at 20°C for maturation,

211 to ensure cation exchange and mixture equilibration occurred prior to stabilisation. For the

212 experimental process, 10% (total mix weight) cement was used to stabilise the contaminated

213 clay, and this was added as slurry with 8% water to the pre-mixed and equilibrated

214 contaminated clay with 1% humic acid. The final mix design contained approximately 89%

215 kaolin clay, 1% humic acid, 500mg/kg zinc, stabilised with 10% CEM II Portland Limestone

216 cement, mixed at 28% (final water content) water content (total mix weight). After

217 stabilisation, the mix was packed in 10cm long 10cm diameter polyvinyl chloride (pvc-u) pipes

218 using vertical compression via an air pump (ENERPAC 10,000psi Turbo II) in three equal

219 layers, at a bulk density of 1600kg/m^3 [should give dry density – 1250kg/m^3]. The pipes were

220 then capped and sealed with silicon sealant to prevent air ingression and stored at 20°C for the

221 required durations prior to testing.

222

223 **Leaching and Extraction Tests**

224 To address the equilibrium and disequilibrium release controlling mechanisms, a suitable suite

225 of leaching tests had to be established, to provide information on components releases under

226 the prevailing constraints. Also, to estimate the amount of reactive hydrous ferric oxide (HFO)

227 surfaces, extractions for oxalate (amorphous aluminium), ascorbate (amorphous iron) and

228 Dithionite (crystalline iron) were undertaken, according to Dzombak and Morel (1990). All

229 chemical leaching or extraction tests and chemical parameter measurements were undertaken at

230 a constant temperature of 20±1°C. The primary leachant employed for testing was

231 demineralised water, obtained through reverse osmosis.

232

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 where 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 8litres 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 was sealed to prevent excessive air interactions, with provisions

248 made for the insertion of flexible plastic pipes for sample collection and replacement.

249

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

258   difference of no more than 1.5 pH units between successive samples at relatively large liquid to

259   solid ratios of 20±1: 1. This liquid to solid ratio is the ratio of leachant to the test specimen,

260   with higher ratios providing a larger volume of leachant relative to the mass of the test

261   specimen. Typically, 10 grams of the solid sample was leached with 200ml of demineralised

262   water and acid or base as required, with the leachant prepared in volumetric flasks using the

263   predetermined amount of acid / base (via titration and equilibration over 24 hours due to the

264   buffering capacity of the specimens) which is added to the primary leachant (demineralised

265   water). Testing was undertaken using an end over end shaker at 10rpm (revolutions per

266   minute), with the leachant added in three steps over two hours. . pH was measured at 4, 44 and

267   48 hours, and a maximum variation of 0.3 pH units was required between 44 and 48 hours to

268   ensure equilibration had been attained during testing.

269

270   **Porewater Leaching**

271   Most leaching tests are carried out at relatively high L/S ratios (such as 20:1 employed for the

272   pH dependent leaching tests), and do not give insight into leaching under often low L/S

273   conditions (porewater) encountered in the field (Van der Sloot *et al.*, 2006). For the current

274   study, the up-flow percolation test CEN/TS 14405 (2008) was employed to evaluate leaching,

275   using eluate obtained from the first 3 fractions of the test up to a cumulative L/S ratio of 0.5.

276   Here, 500ml of demineralised water will be passed through 1kg of the test sample. Samples

277   were crushed under controlled conditions to prevent excessive aeration and carbonation, and

278   tested in 32cm long 10 cm diameter cylindrical columns at a flow rate of 48ml/h. Prior to

279   testing, samples were saturated with demineralised water, and allowed to stand for 4 days to

280   reach equilibrium conditions. The first two fractions (0.1 L/S each) were used for validation

281   that equilibration of the samples have been attained, and should not vary by more than 0.5 pH

282   units. If conditions were met, the two fractions were combined to form one sample (cumulative

283   0.2 L/S fraction) prior to analysis.

284

Hydrous Ferric Oxide (HFO) Extraction

HFO extractions were undertaken along the guidelines prescribed by Dzombak and Morel

(1990), using the ascorbate extraction method to determine the amorphous iron content, the

dithionite extraction method to determine the crystalline iron content, and the oxalate

extraction method to determine the amorphous aluminium content. For modelling purposes,

amorphous aluminium is treated similar to amorphous iron, where 1mol amorphous iron ≈

1mol amorphous aluminium (Dijkstra *et al.,* 2004), using recommended specific surface areas

of 600m^2/g for aluminium and 100m^2/g for crystalline iron (Meima and Comans, 1998).

Results for HFO (iron and amorphous aluminium) used as part of modelling inputs are

presented in Table 2. Kaolin dissociates under alkalinity with gibbsite becoming stable through

silica loss (Langmuir, 1997), and thus HFO content may change with hydration. However, for

the current study, measurements were taken at 150 days, and assumptions of constant HFO

content made for consistency.

Table 2

Leaching Assessments and Modelling Tools

Leaching assessments were undertaken using the leaching expert system and database

LeachXS, embedded with the geochemical speciation modelling tool ORCHESTRA (Van der

Sloot *et al.,* 2007). ORCHESTRA uses geochemical information from the extended

MINTEQA2 database (US EPA speciation database), models organic carbon interactions using

the NICA-Donnan model (Van der Sloot *et al.,* 2005), and models sorption to HFO according

to the generalised 2 layer model of Dzombak and Morel (1990). Leaching information from the

different tests, material properties, leaching parameters, and extraction information were input

into LeachXS, from where leaching evaluations were undertaken. Speciation determinations

310 (via embedded ORCHESTRA) were then undertaken, and the relevant mineral phases selected

311 based on expected mineralogy of the stabilised matrix under the prevailing conditions prior to

312 modelling. LeachXS – ORCHESTRA combination provides quick data retrieval, automatic

313 input generation for modelling, processing of calculated results and data presentations (Van der

314 Sloot *et al.,* 2005). It allows updating and modification of speciation information, expansion of

315 the thermodynamic database, a constantly expanding repository of speciation and leaching, and

316 is ultimately a holistic platform for undertaking qualitative and quantitative leach assessments.

317

318 **LEACHING ASSESSMENTS AND GEOCHEMICAL MODELLING**

319 Eluates from the different chemical leaching tests and extractions were undertaken using an

320 ICP-OES (inductively couple plasma – optical emissions spectroscopy) for cation analyses,

321 and using a Shimatzu high sensitivity organic carbon analyser for dissolved organic carbon

322 (DOC) measurements. Table 3 shows the detection limit of the ICP-OES equipment for the

323 elements presented, and the measure of total organic carbon used for modelling was the

324 volume added to make 1% humic acid considering the low organic carbon of the utilised kaolin

325 clay. Leaching evaluations were then undertaken using LeachXS for the stabilised zinc

326 contaminated kaolin clay with 1% humic acid (denoted by EOHZ) to determine the

327 effectiveness of treatment, chemical durability and changes in these properties with hydration.

328 To evaluate the implications of the increased organic content on the contained zinc, findings

329 and results were compared to those for a comparable matrix without increased organic content

330 (John *et al.,* 2011a). Results required for the comparison of cumulative release and component

331 availability without the additives (denoted by EOZ) are included for the different hydration

332 durations (28, 150 and 300 days).

333

334 *Table 3*

335

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

361   measured concentrations in analysed eluates, and graphs are presented in log scale to capture

362   the range of concentrations and time (Figure 4b) presented.

363   From the evaluation of porewater leachability at low L/S ratios (CEN/TS 14405, 2008), it was

364   observed that zinc was not readily mobilised from the stabilised matrix under the prevailing

365   chemical conditions (all measurements below detection limit), while aluminium and silicon

366   release were minimal. These results are thus not presented within this report, but were included

367   during speciation modelling to determine the relevant solubility controlling mineral phases.

368

369   *Table 4*

370

371   *Figure 4*

372

373   Considering kaolin dissociates in alkaline conditions, it was important to evaluate durability in

374   view of the structural components for the kaolinite [$Al_2Si_2O_5$ $(OH)_4$]. Time dependent

375   cumulative releases indicate increasing aluminium availability with increasing [over a period

376   up to 300 days) hydration, further suggesting an increasing of dissociation during this process.

377   Silicon and calcium availability, however, decreased with hydration (Table 4) (over a period up

378   to 300 days) due to silicic acid (H_4SiO_4)-calcium complexes forming stable cementitious

379   minerals. Table 5 shows the maximum availability of the selected components during pH

380   dependent leaching, and indicates that less than 1% of the total structural cations (85% alumina

381   and silica or 40% aluminium and silicon present in kaolin clay) are available for release from

382   the stabilised material. This indicates that the availability of dissolution product decreases at

383   increased hydration durations, which suggests that even though dissociation is taking place, the

384   products are used up for formation of stable mineral precipitates. This is consistent with

385   observation on stabilised clay soils made by Bell (1996), McKinley *et al.* (2001) and Bone *et*

386   *al.* (2004). Figure 5 shows the time dependent leaching and cumulative releases of silicon and

387 aluminium at the different hydration durations. The pH dependent leaching trends for

388 aluminium and silicon are presented in Figure 6 at the different hydration times. These results

389 are presented to show concentrations in the analysed eluates, and are also presented in log scale

390 to capture the range of time (Figure 5) and concentrations (Figure 6) covered. The change in

391 the leachability of silicon and aluminium (Figure 5A and 5C) drop sharply at 19 days due to

392 the short leachant renewal period. The pH dependent trends (Figure 6) were not significantly

393 different at the range of time periods examined, but the solubility of aluminium (under neutral

394 conditions; Figure 6A) is influenced by the presence of gibbsite resulting from kaolin

395 dissociation. Modelling indicated that the solubility of aluminium was controlled by kaolinite,

396 montmorillonite, gibbsite, hydrated calcium aluminosilicates, hydrated calcium aluminates,

397 ettringite and organic matter; whereas silicon was controlled by kaolinite, jennite, calcium

398 silicate hydrate, hydrated calcium aluminates, hydrous ferric oxides and zinc silicates.

399

400 *Table 5*

401 *Figure 5*

402 *Figure 6*

403

404 **Zinc Containment**

405 Table 4 shows that zinc was not leached over time under the material's natural conditions.

406 Table 5 shows that the availability of zinc decreases with increasing period of hydration.

407 Kaolin clay with additives (EOHZ), had increased zinc availability at early age, but this

408 decreased with time up to 300 days, when results were comparable to the control mixture.

409 Also, at 28 days of hydration almost all introduced zinc is available for leaching (0.5grams/kg).

410 Zinc silicates are likely to prevail with presence of silicic acid in the pore solution and

411 aluminium in the crystalline lattice (McPhail *et al.,* 2003), and the presence of increased

412 organic containment retards cement hydration (Bone *et al.,* 2004). This retardation is likely due

413   to hydration when more stable products form through decreased kaolin dissociation and

414   complexation of zinc with organic carbon, which are responsible for the increased availability

415   in the humic acid matrices. As hydration progresses past this retardation, more silicic acid

416   becomes available in the pore solution for complexation with zinc, and more zinc is complexed

417   with the formed cementitious products, which induced increased containment as seen at the

418   advanced hydration period (Table 5).

419

420   Zinc may be incorporated by the kaolin clay to form a range of potential species. Fraipontite -

421    $(Zn, Al)_3(Al, Si)_2O_5(OH)_4)$, complexed with calcium to form calcium zincate, orprecipitated as

422   insoluble zinc silicates. Predictions of speciation also suggest a range of zinc silicates can be

423   formed: metastable zinc silicate $(ZnSiO_3,)$ complexes with magnesium $(Zn,Mg)Si_2O_6$, as

424   Willemite - Zn_2SiO_4, or as hydrated hermimorphite $Zn_4Si_2O_7(OH)_2.H_2O$. Under the prevailing

425   conditions, it was expected that all these mineral formations are possible, but some like

426   hermimorphite and fraipontite lack sufficient thermodynamic information for use in modelling

427   (McPhail *et al.,* 2003). These phases were not available for selection during speciation

428   determinations, and for consistency $ZnSiO_3$ was used to represent all zinc silicates. The use of

429    $ZnSiO_3$ was also seen in similar modelling work by Comans *et al* (1993) and Meima and

430   Comans (1999), and in both cases amphoteric leaching was observed for zinc releases.

431   However, this was not observed during the current study (Figure 4A), but was comparable to

432   observations of zinc leaching in Hale *et al.* (2012). Figure 7 shows the geochemical speciation

433   modelling predicted and measured releases for zinc, and the predicted solubility controlling

434   mineral phases at the different hydration durations for the stabilised zinc contaminated kaolin

435   clay with 1% humic acid.

436

437   *Figure 7*

438

439   These results show predictions for amphoteric leaching, but the measured trends consistently

440   show that zinc was insoluble. Considering the reduced silica solubility observed for the matrix

441   under alkaline conditions (Figure 6B), it is likely that zinc is complexed as an insoluble

442   silicate, such as hermimorphite, for which thermodynamic information is not available.

443   The predictions (Figures 7B, 7D and 7F) show that zinc solubility is controlled by zinc

444   silicates, franklinite, calcium zincate, particulate organic matter, and to a lesser degree HFO.

445   By way of interest, Franklinite is a mineral found in granitic rocks from which kaolin clays are

446   weathered.

447

448   Figure 8 shows the pH dependent releases of DOC with increasing hydration, which will be

449   dependent on the properties of the utilised humic acid. The results are presented in g/kg,

450   converted to show the releases from the mass of sample, rather than the release into the eluates.

451   The results show that DOC has lower solubility under both alkaline and acidic conditions, with

452   the higher solubility under neutral conditions. However, while DOC releases were elevated

453   under neutral conditions, this did not modify the zinc leachability trend (Figure 4A).

454

455   *Figure 8*

456

457   The approach presented in this paper demonstrates how longer term stability of S/S has been

458   evaluated for a zinc contaminated kaolin soil, treated using cement. This work demonstrates

459   the potential for such analysis to be extended for all S/S used in the treatment of soil containing

460   any heavy metal contamination. Thus to fully understand and therefore design S/S for the

461   longer term, knowledge of the release controlling mechanisms, mineralogy, field exposure

462   conditions, and key extrinsic parameters, such as hydrological, redox and, weathering

463   conditions are required. This is achieved through leaching assessments augmented by

464   geochemical speciation modelling a complete assessment can be made.

465

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

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_2O_3 – Aluminium Oxide	4.3
Quartz	1-2	Fe_2O_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_2O – 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.*

		Aluminium	Total Iron	Crystalline Iron	HFO (kg/kg)
Sample	**Extraction**		(mol/kg)		
	Ascorbate		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.

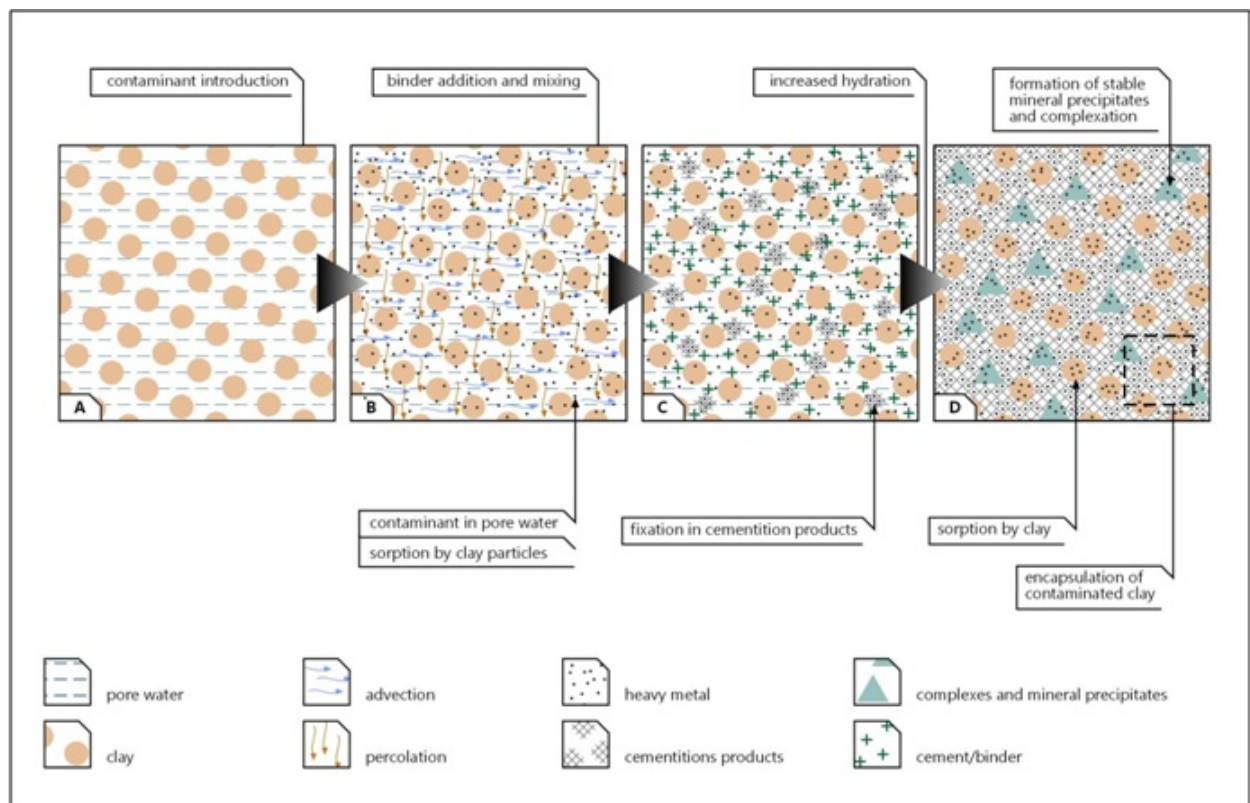| Zinc Samples Cumulative Releases (g/m^2)				
Sample	Al	Si	Ca	Zn
EOZ 28days	3.72	3.91	142.70	0.0004
EOZ 150days	5.33	3.63	61.13	0.0004
EOZ 300days	7.36	3.53	64.63	0.0010
EOHZ 28days	2.29	4.78	185.14	0.0060
EOHZ 150days	4.24	3.78	134.65	0.0009
EOHZ 300days	6.21	3.72	94.05	0.0030

Figure 1: Conceptualisation of binder application process and formations of containment products with increasing hydration (John, 2011)
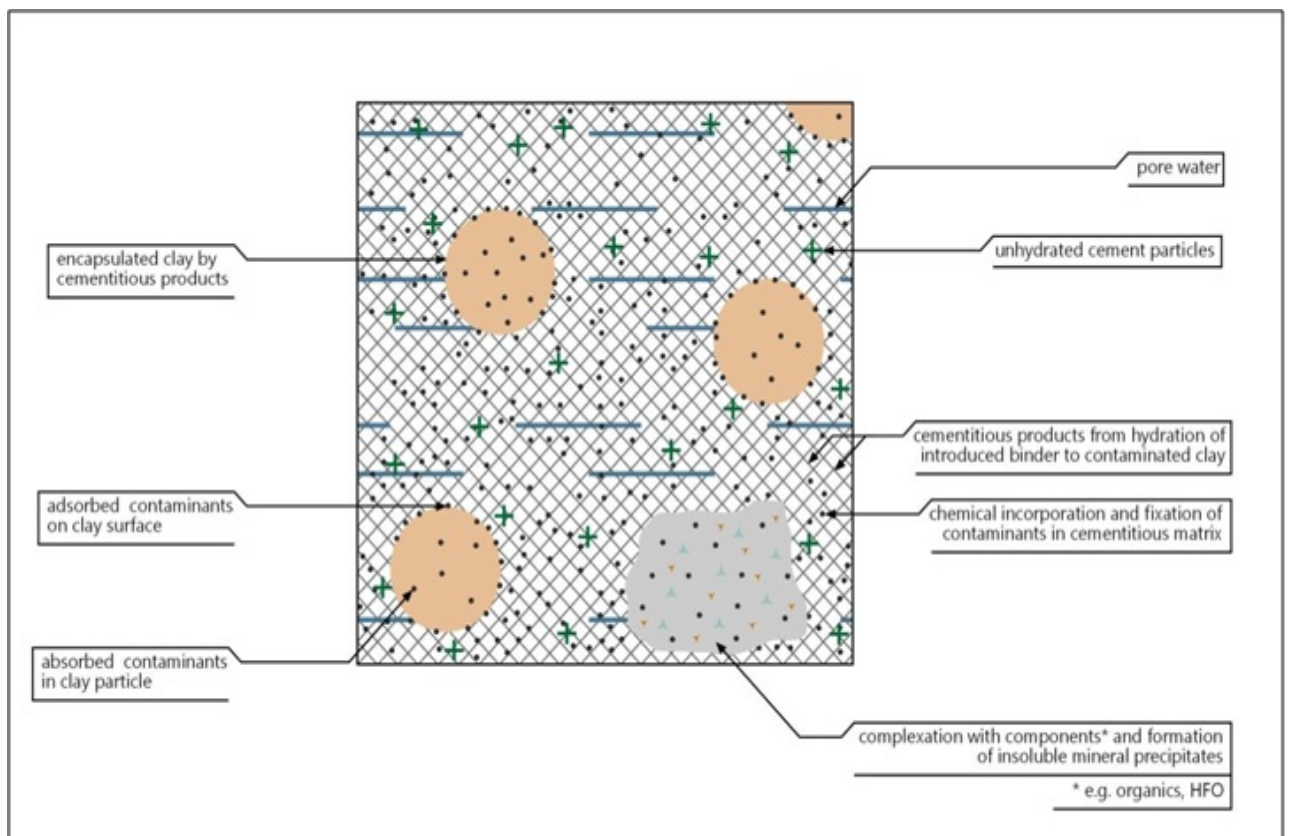
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Figure 2: Contaminant containment mechanisms within the stabilised material (John, 2011)
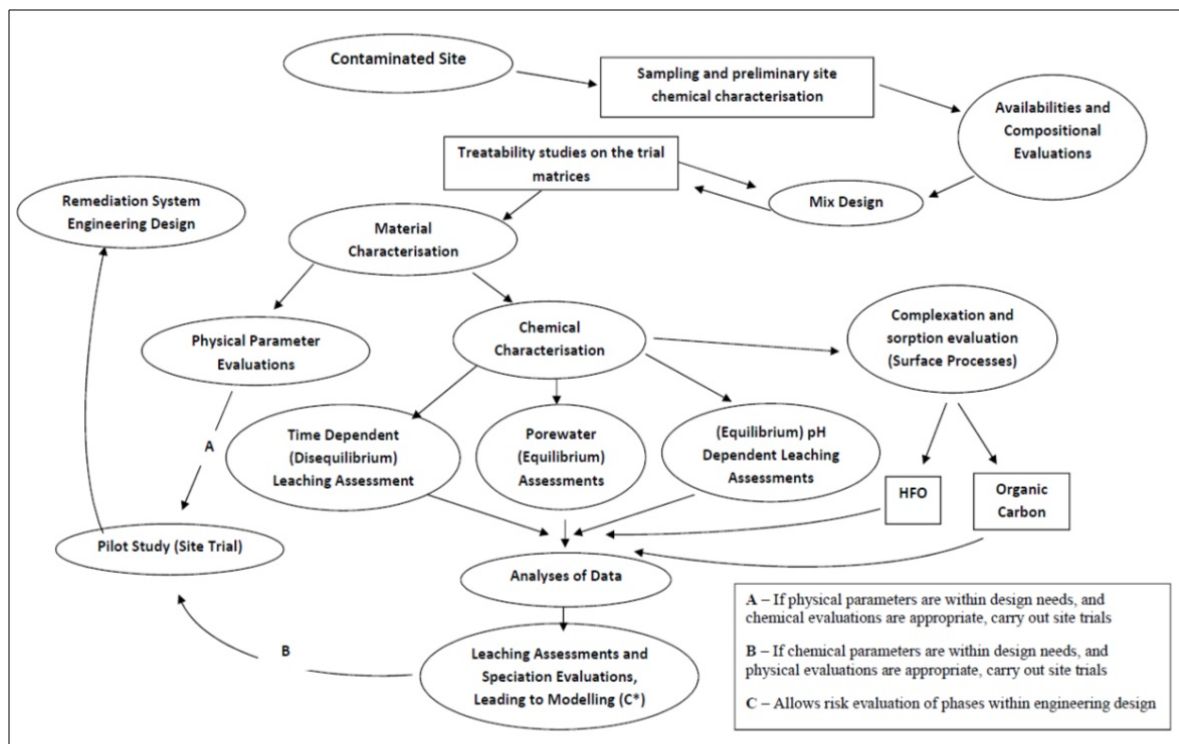
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692   Figure 3: Requirements for material characterisation and evaluation of effectiveness during S/S design, highlighting the chemical characterisation processes (John, 2011)
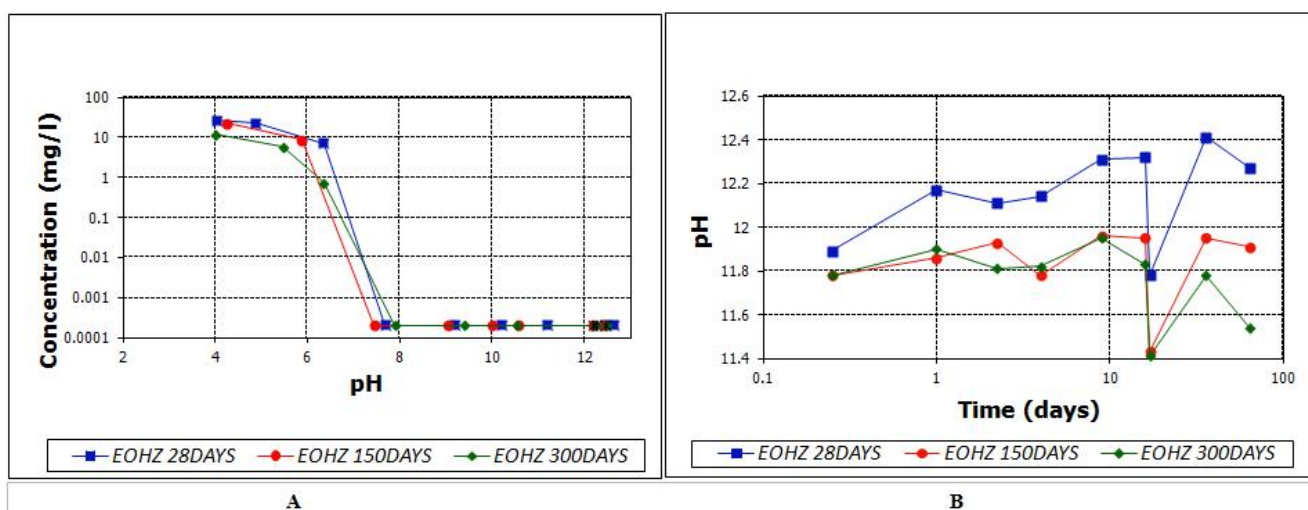
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Figure 4: (A) pH dependent leaching of zinc from stabilised zinc contaminated kaolin clay with 1% humic acid. (B) pH evolution during evaluations of time dependent leaching for stabilised zinc contaminated kaolin clay with 1% humic acid.
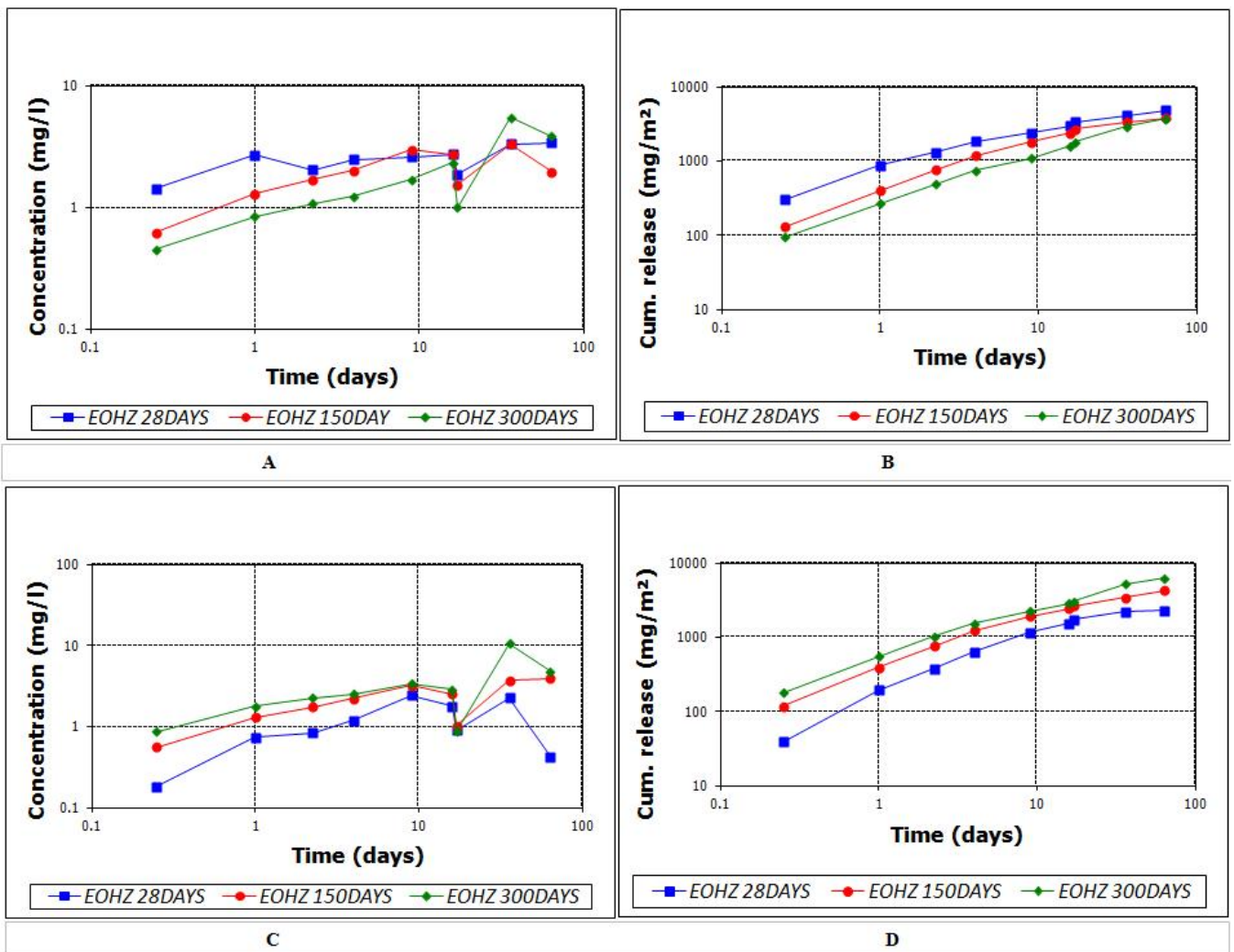
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Figure 5: (**A**) Releases of silicon during time dependent leaching evaluations for stabilised zinc contaminated kaolin clay with 1% humic acid (EOHZ). (**B**) Cumulative release of silicon during time dependent leaching evaluations for EOHZ. (**C**) Releases of aluminium during time dependent leaching evaluations for EOHZ. (**D**) Cumulative release of aluminium during time dependent leaching evaluations for EOHZ.
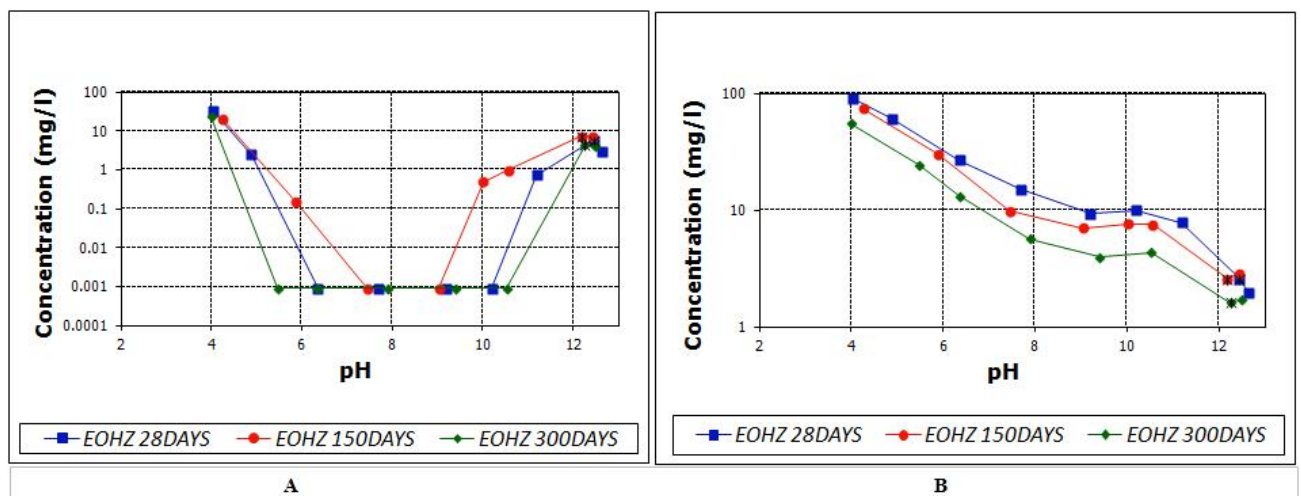
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Figure 6: (**A**) pH dependent leaching of aluminium from stabilised zinc contaminated kaolin clay with 1% humic acid at the different hydration durations. (**B**) pH dependent leaching of silicon from stabilised zinc contaminated kaolin clay with 1% humic acid at the different hydration durations.
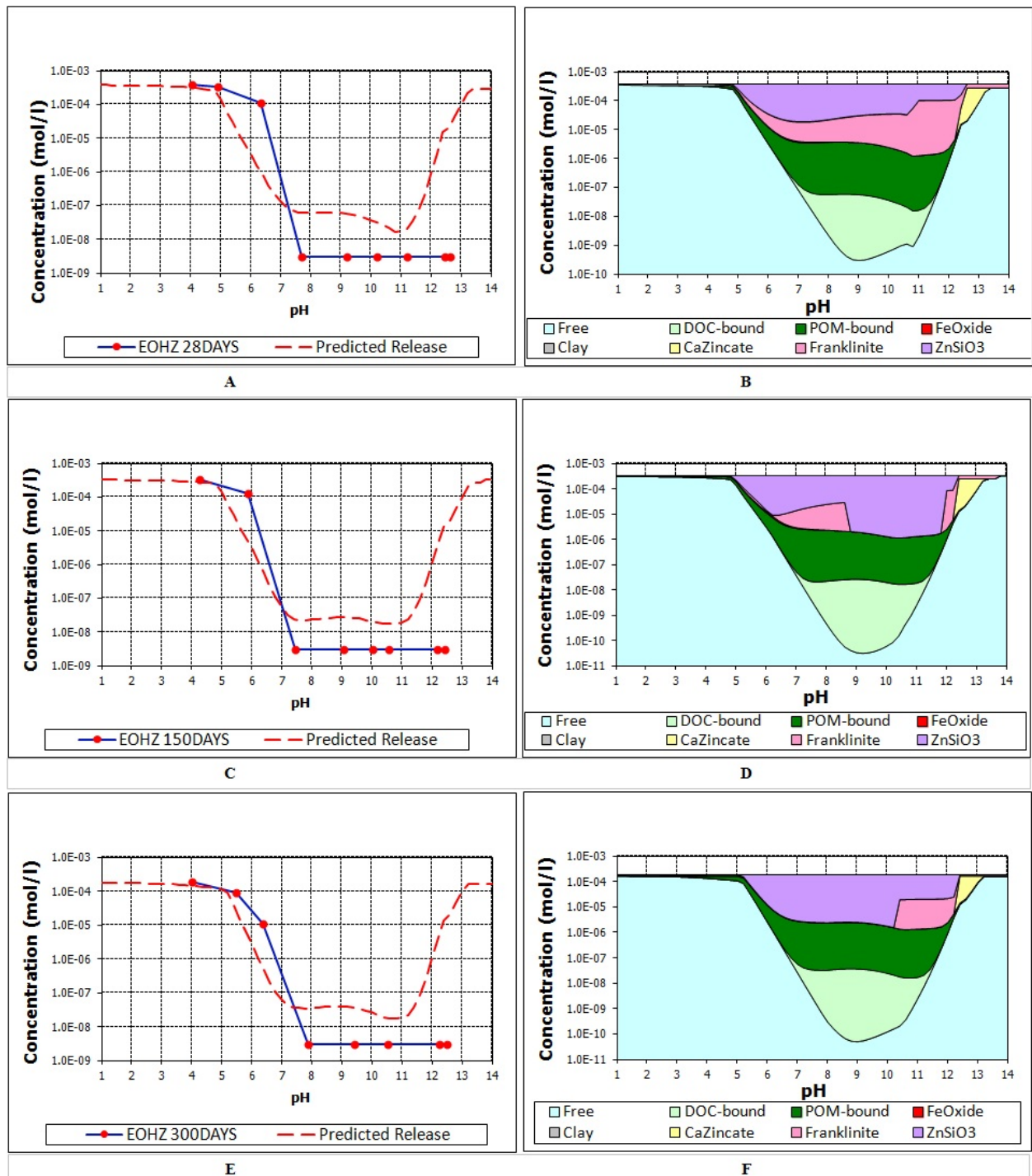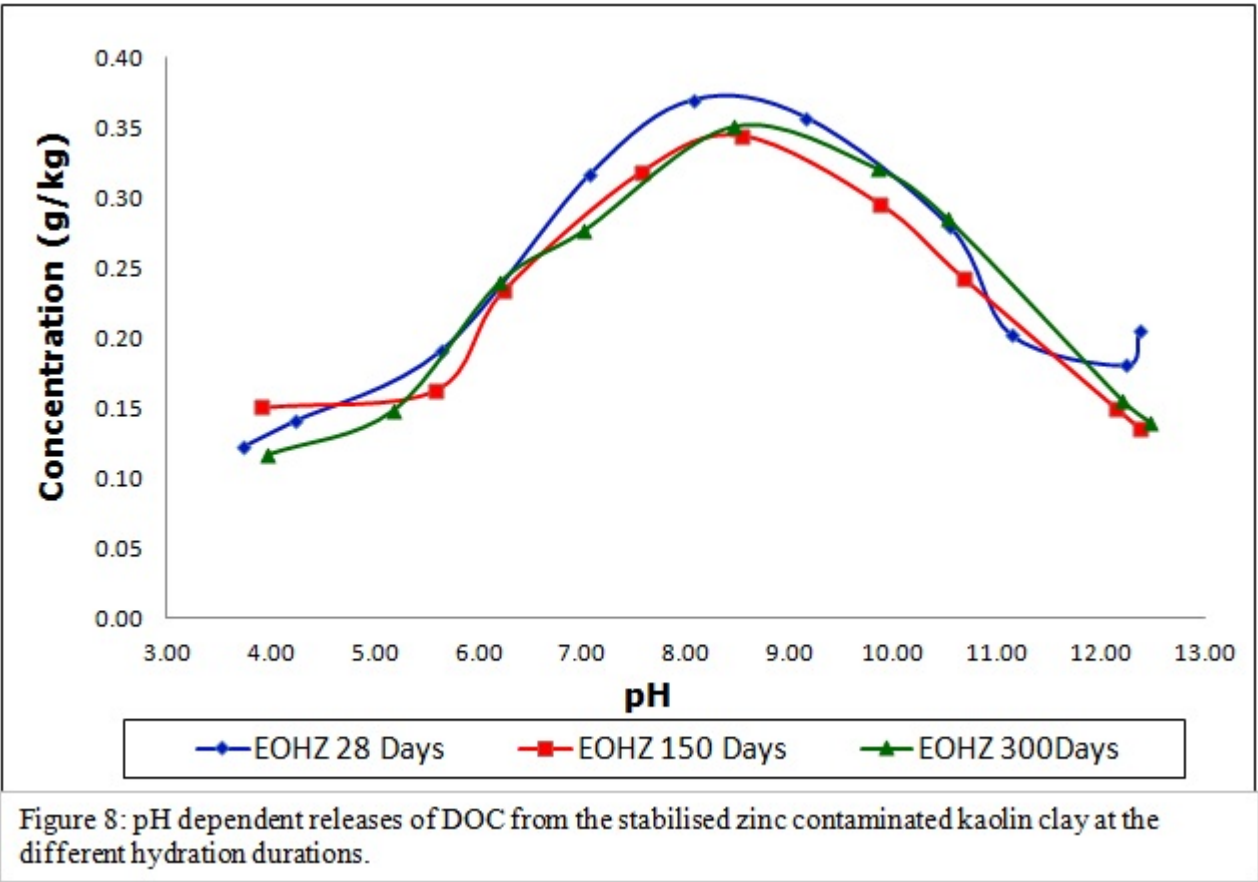
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Figure 7: (**A**) Measured and predicted leaching of zinc leaching at 28 days hydration. (**B**) Predicted solubility controlling mineral phases for zinc at 28 days hydration. (**C**) Measured and predicted leaching of zinc leaching at 150 days hydration. (**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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