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

2

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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

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

28

29 **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

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

154 acid. The clay used was PolWhite-E kaolin clay, containing >85% alumina and silica (40%
155 aluminium and silicon), with 40% of particles $\leq 2\mu\text{m}$ and <10% of particles $\geq 10\mu\text{m}$. 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/m³ [should give dry density – 1250kg/m³]. The pipes were
220 then capped and sealed with silicon sealant to prevent air ingress-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

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 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 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

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

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

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

336 **Chemical Durability**

337 To evaluate chemical durability, two key factors were considered: the stability of the
338 contaminants under prevailing chemical conditions; and the stability of the structural cations
339 for the kaolin clay (aluminium and silicon). Table 4 shows the time dependent cumulative
340 release of elements (Al, Si and Zn) from monolithic test specimens, including calcium, for
341 comparison with the stabilised mixture without humic acid, at the different hydration durations.
342 These results are presented in grams per square meter of the measured surface area, for
343 leaching due to chemical kinetics with time, via diffusion, dissolution and surface wash off
344 from the stabilised materials natural chemical conditions (CEN/TS 15863, 2008). It is
345 important to understand that the releases of zinc were in trace amounts, where 0.004g/m²
346 observed for EOZ at 28 and 150 days represent the cumulative measure for the zinc detection
347 limits of the equipment, which was used as the minimum value rather than zero. Zinc release
348 was not observed under alkaline conditions during pH dependent leaching assessments, at the
349 different periods of hydration (Figure 4a). This confirms the observations from the time
350 dependent leaching assessments from monolith assessments, at the stabilised materials natural
351 chemical conditions. However, theoretical solubility of zinc as a hydroxide should yield an
352 amphoteric (higher leachability at both high and low pH, and lower leachability under neutral
353 conditions) leaching trend, which was not observed for the stabilised matrices. This was likely
354 due to speciation of the mineral precipitates, a trend also observed from leaching data in Hale
355 *et al.* (2012), for leaching from 15% cement stabilised contaminated soils. Figure 4b shows the
356 evolution of pH during time dependent leaching for monolithic stabilised zinc contaminated
357 kaolin clay with 1% humic acid at the different durations of hydration. This test was
358 undertaken on monolithic specimens at the stabilised materials natural chemical conditions
359 using demineralised water, and the presented pH shows the evolutions in measured pH for
360 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 $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$. 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 $(\text{Zn, Al})_3(\text{Al, Si})_2\text{O}_5(\text{OH})_4$, complexed with calcium to form calcium zincate, or precipitated 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 $(\text{Zn, Mg})\text{Si}_2\text{O}_6$, as
424 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
425 conditions, it was expected that all these mineral formations are possible, but some like
426 hercynite 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 hercynite, 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

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

485 **Acknowledgements:** Special thanks to Hans Van der Sloot for assistance with getting to grips
486 with the leaching assessment and modelling tool. Thanks also to Dr Angela Williams and
487 Diane Spencer of University of Wolverhampton SAS for analytical assistance.

488

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642 Table 1: Mineral compositions of kaolin clay (PolWhite-E) and CEM II Portland limestone
 643 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

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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		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

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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

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

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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

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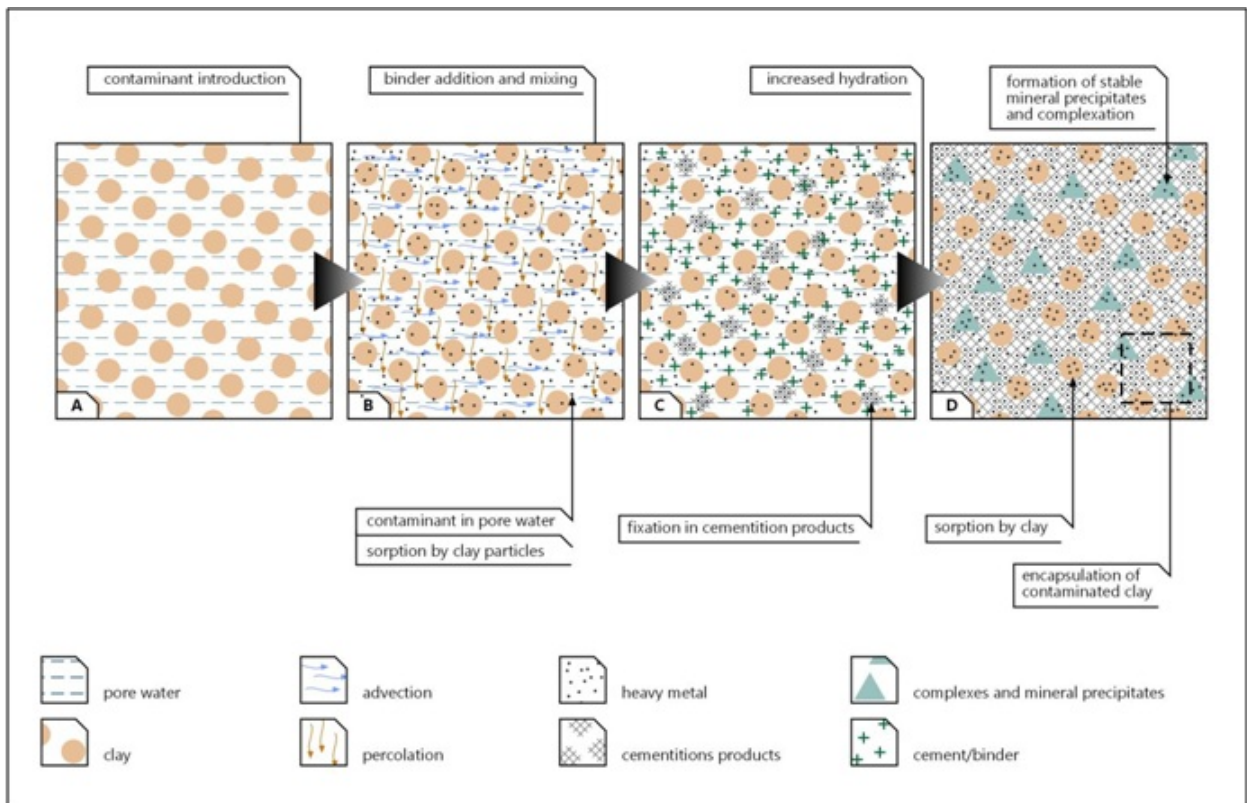


Figure 1: Conceptualisation of binder application process and formations of containment products with increasing hydration (John, 2011)

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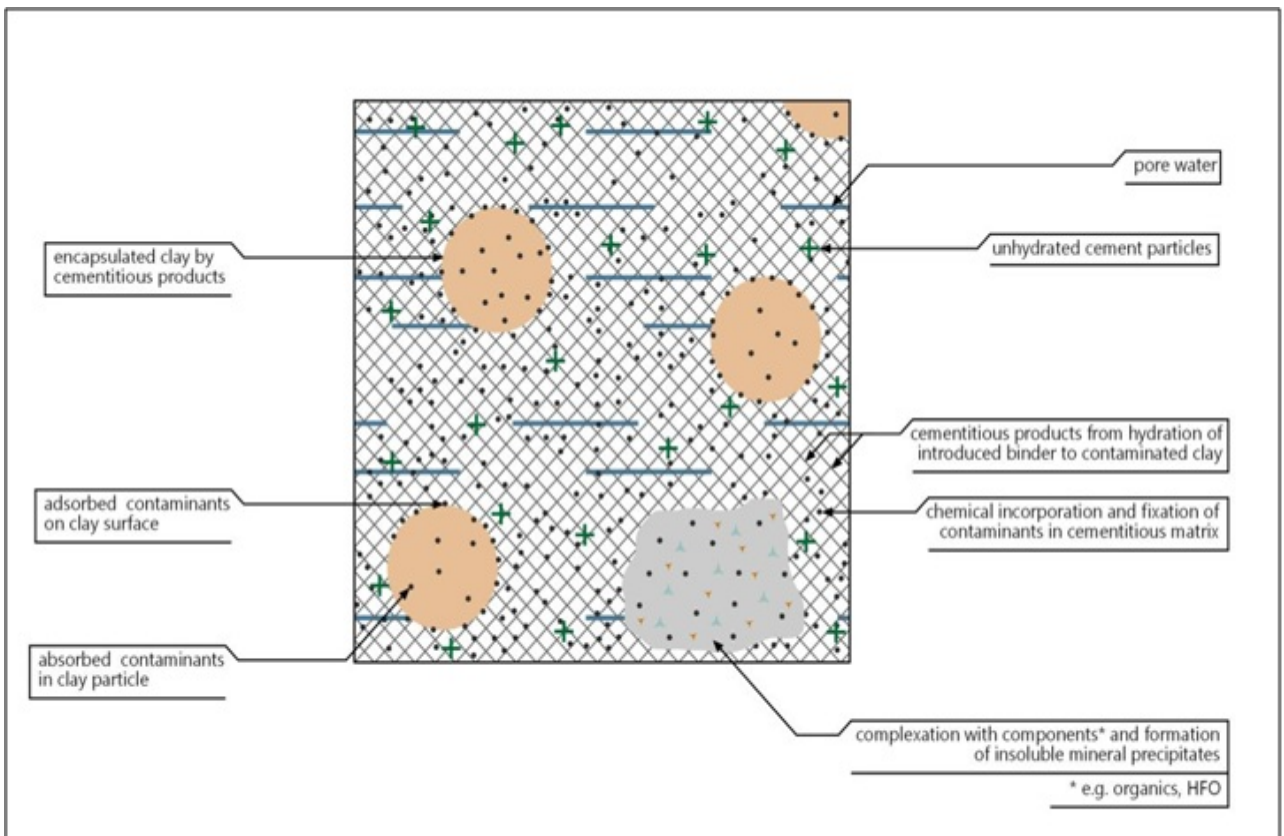


Figure 2: Contaminant containment mechanisms within the stabilised material (John, 2011)

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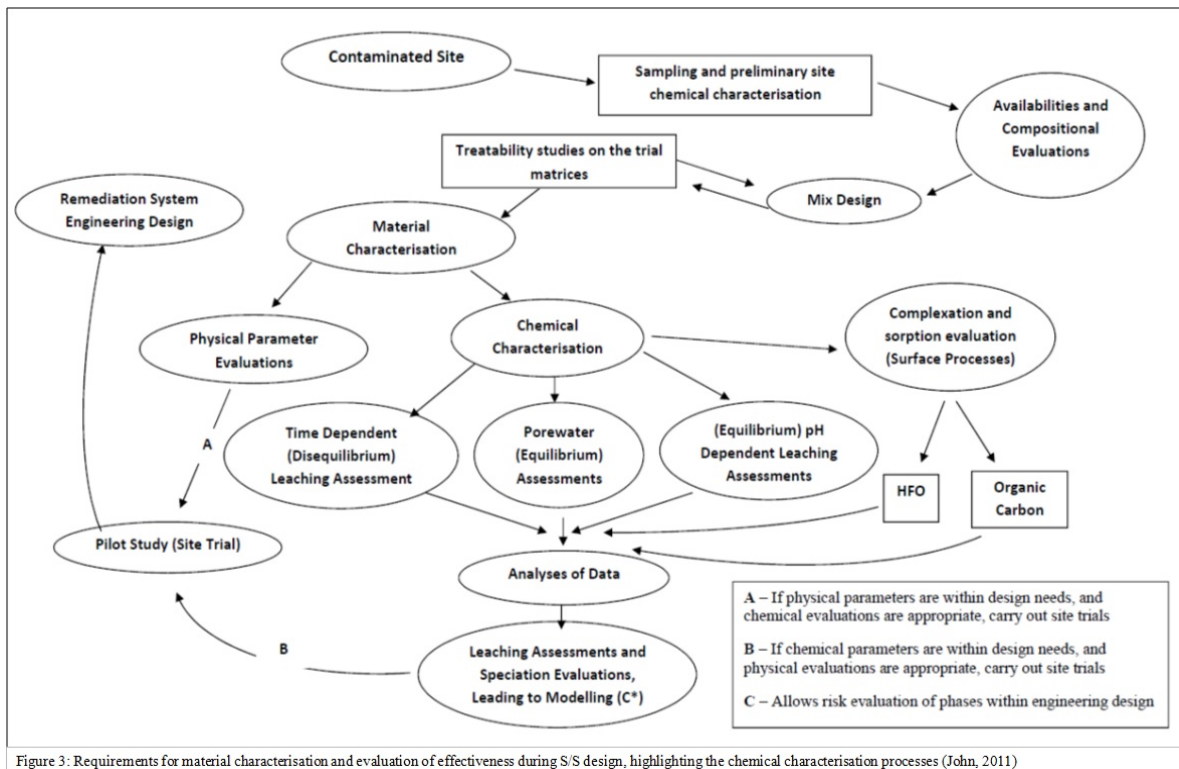


Figure 3: Requirements for material characterisation and evaluation of effectiveness during S/S design, highlighting the chemical characterisation processes (John, 2011)

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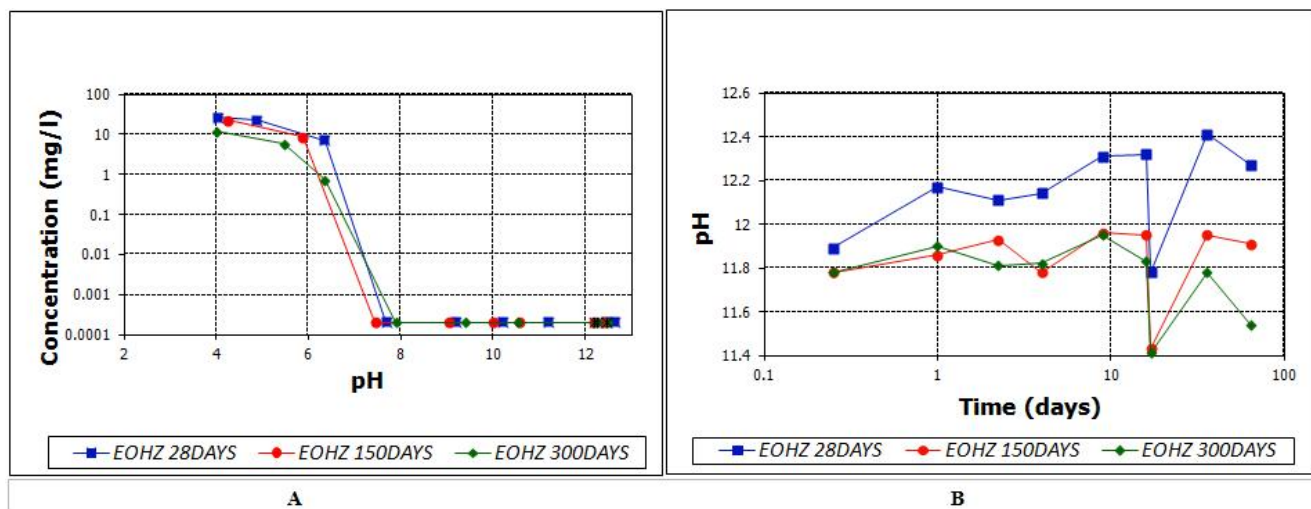


Figure 4: (A) pH dependent leaching of zinc from stabilised zinc contaminated kaolin clay with 1% humic acid. (B) pH evolution during evaluations of time dependent leaching for stabilised zinc contaminated kaolin clay with 1% humic acid.

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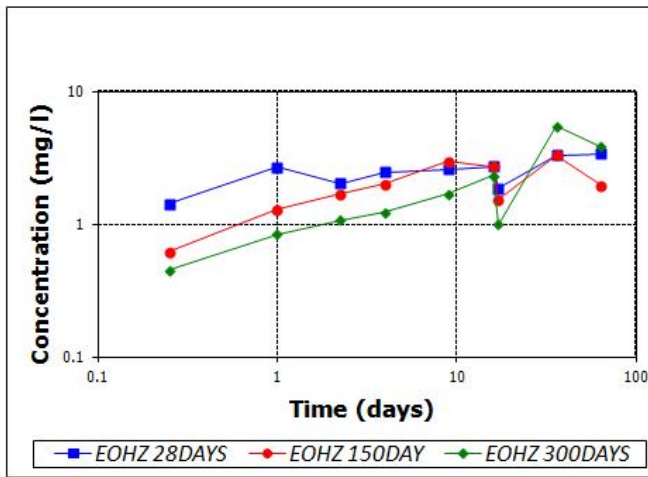
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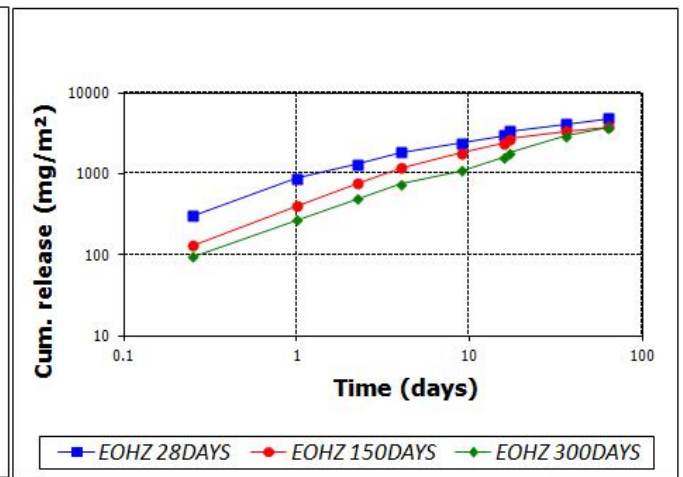
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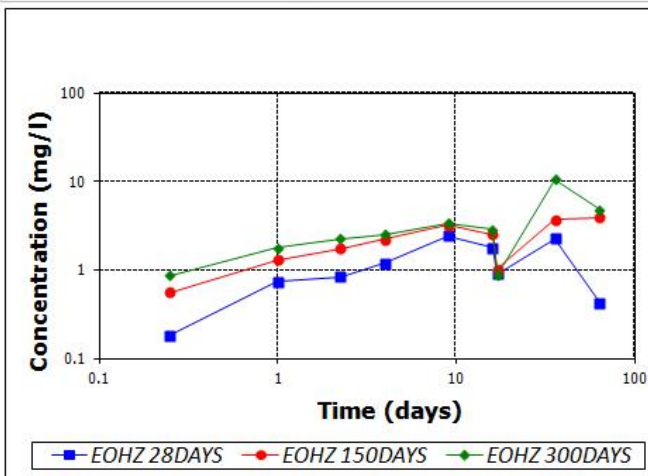
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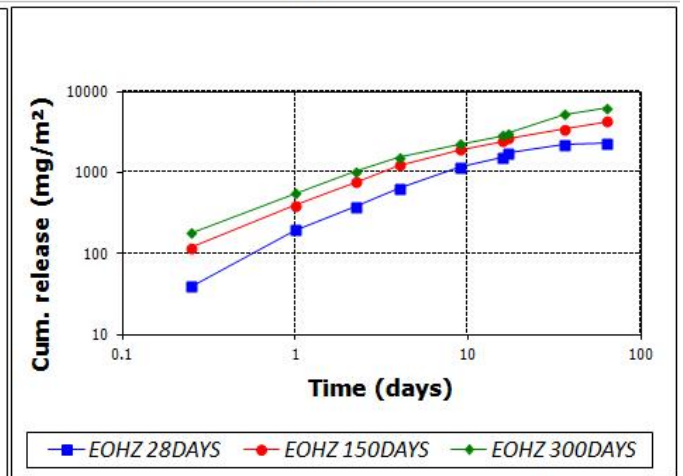
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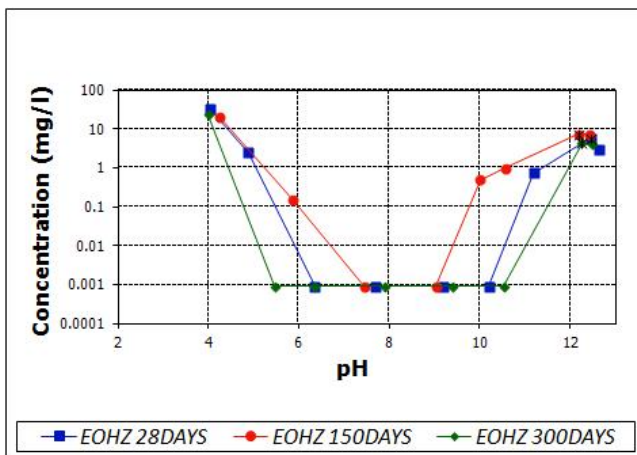
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Figure 5: (A) Releases of silicon during time dependent leaching evaluations for stabilised zinc contaminated kaolin clay with 1% humic acid (EOHZ). (B) Cumulative release of silicon during time dependent leaching evaluations for EOHZ. (C) Releases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

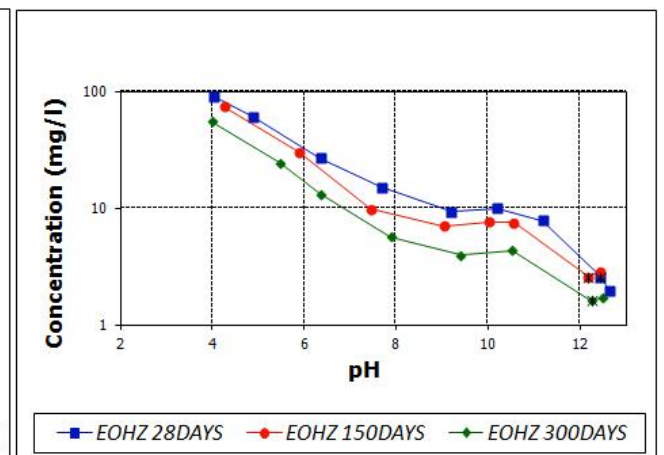
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Figure 6: (A) pH dependent leaching of aluminium from stabilised zinc contaminated kaolin clay with 1% humic acid at the different hydration durations. (B) pH dependent leaching of silicon from stabilised zinc contaminated kaolin clay with 1% humic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

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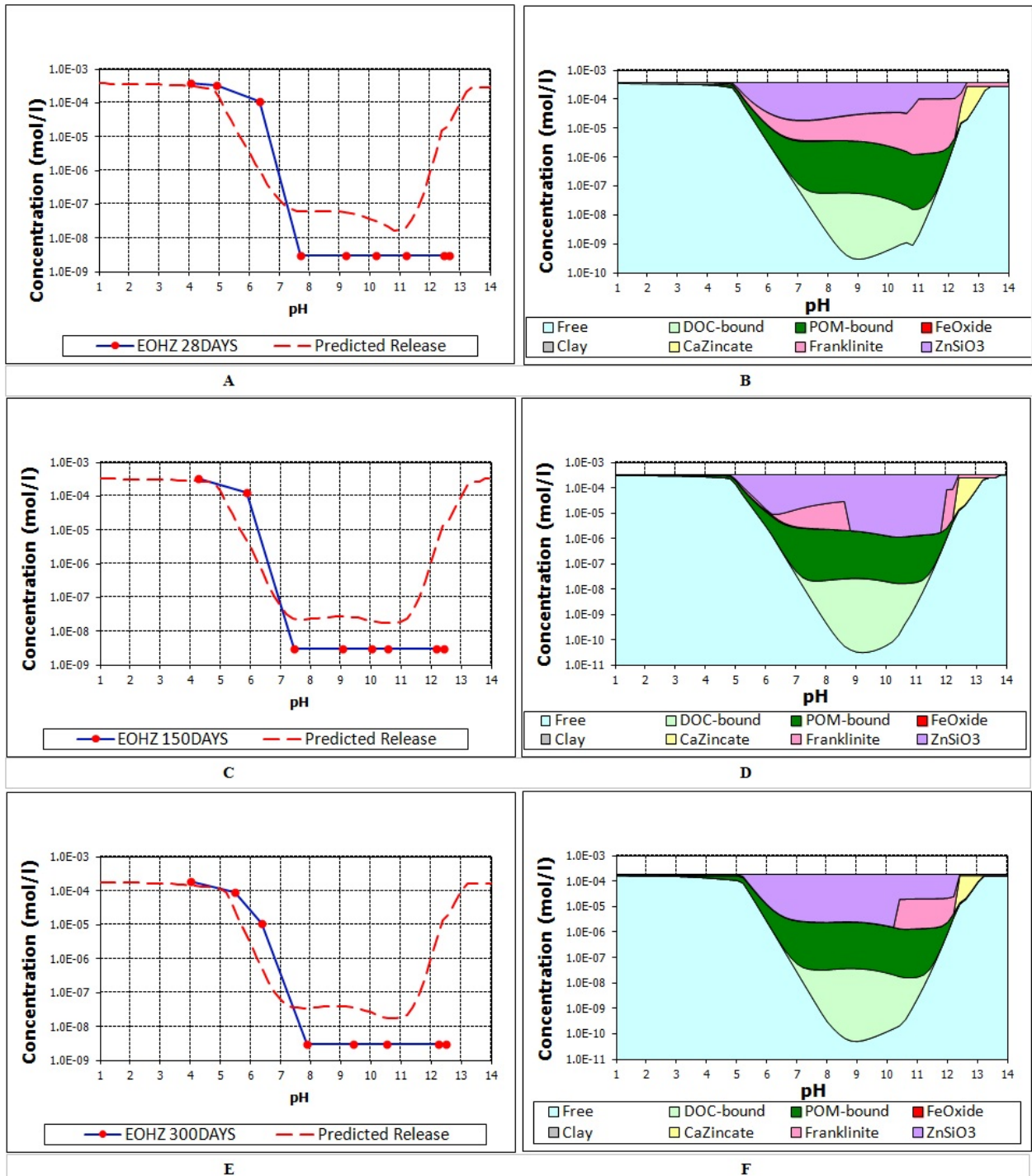


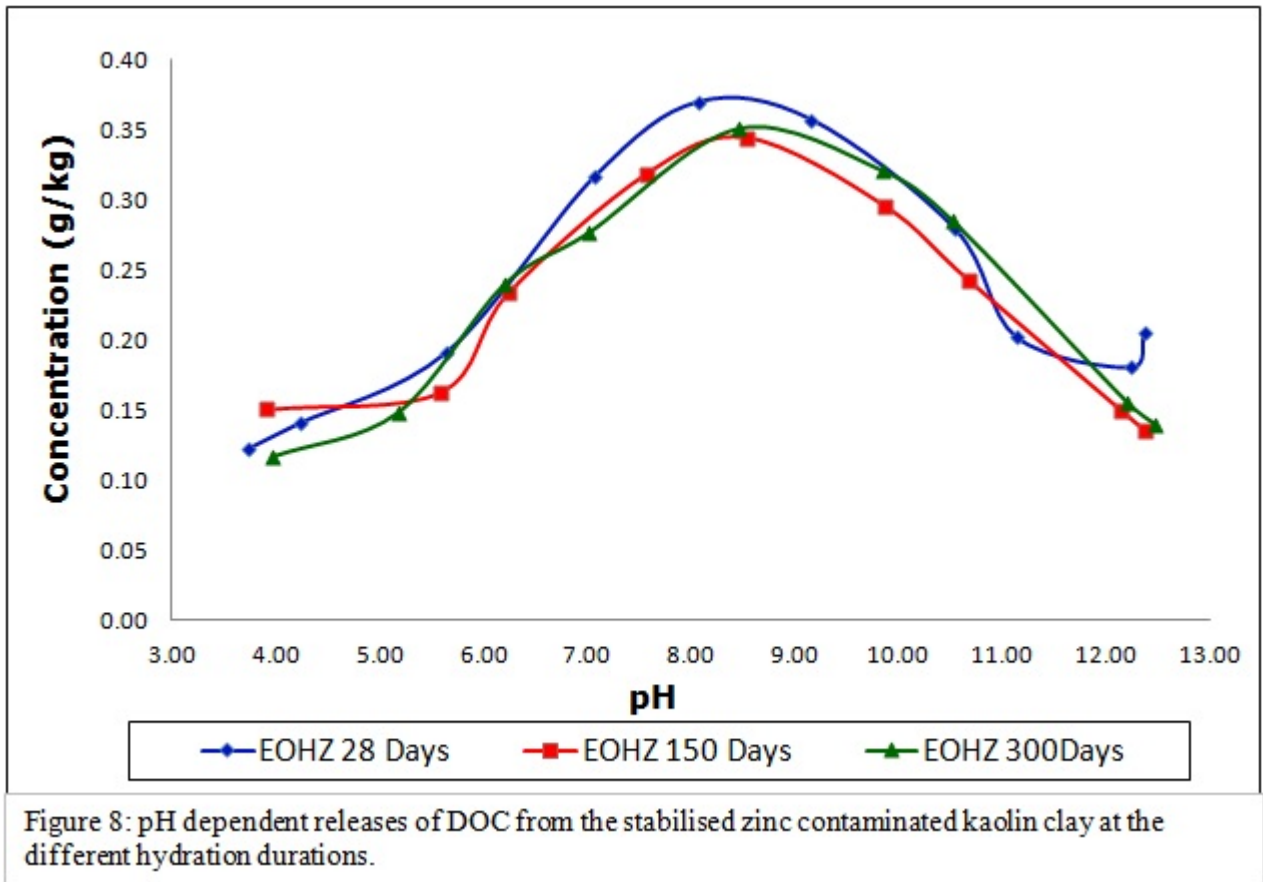
Figure 7: (A) Measured and predicted leaching of zinc leaching at 28 days hydration. (B) Predicted solubility controlling mineral phases for zinc at 28 days hydration. (C) Measured and predicted leaching of zinc leaching at 150 days hydration. (D) Predicted solubility controlling mineral phases for zinc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