

19 **Abstract**

20 Coagulation in drinking water treatment has relied upon iron (Fe) and aluminium (Al) salts
21 throughout the last century to provide the bulk removal of contaminants from source waters
22 containing natural organic matter (NOM). However, there is now a need for improved
23 treatment of these waters as their quality deteriorates and water quality standards become
24 more difficult to achieve. Alternative coagulant chemicals offer a simple and inexpensive
25 way of doing this. In this work a novel zirconium (Zr) coagulant was compared against
26 traditional Fe and Al coagulants. The Zr coagulant was able to provide between 46 and 150%
27 lower dissolved organic carbon (DOC) residual in comparison to the best traditional
28 coagulant (Fe). In addition floc properties were significantly improved with larger and
29 stronger flocs forming when the Zr coagulant was used with the median floc sizes being 930
30 μm for Zr; 710 μm for Fe and 450 μm for Al. In pilot scale experiments, a similar improved
31 NOM and particle removal was observed. The results show that when optimised for
32 combined DOC removal and low residual turbidity, the Zr coagulant out-performed the other
33 coagulants tested at both bench and pilot scale.

34

35 **KEYWORDS:** Natural organic matter; NOM; coagulation; water treatment; flocs; floc
36 strength; coagulants; zirconium

37

38. 1. INTRODUCTION

39 Coagulation by hydrolysing metal salts, typically of iron (Fe) or aluminium (Al), is the main
40 reaction stage that drives the removal of natural organic matter (NOM) and other
41 contaminants in potable water treatment. Recent work reconsidering the description of
42 coagulation pathways has suggested that NOM is removed through a combination of direct
43 precipitation of metal-NOM solids and adsorption onto metal hydroxide precipitates (Shin et
44 al., 2008). In both cases the demand for coagulant is stoichiometric and that whenever NOM
45 is present in a source water these two mechanisms dominate. The role of the coagulant
46 depends on many factors including: speciation of the hydrolysis products, quantity and
47 reactivity of complexing ligands, and the rate of mass transfer between these components
48 (Shin et al., 2008). Consequently, the choice of coagulant has a major influence on
49 performance with reported comparisons indicating that, in the case of NOM removal, Fe
50 based coagulants remove approximately 0.5 mg.L^{-1} more dissolved organic carbon (DOC)
51 than Al versions under optimised conditions (Eikebrokk, 1999; Matilainen et al., 2005; Jarvis
52 et al., 2008). The reason for this difference is linked to the distribution of charged hydrolysis
53 species (Johnson and Amirtharajah, 1983; Hundt and O'Melia, 1988; Edzwald and Tobiason,
54 1999) but difficulties persist in identifying all of these forms and the complexity of the
55 reactions of the coagulant with NOM have meant work is usually based on indirect
56 measurements and theoretical calculation of speciation. Nonetheless, the general view is that
57 the maximum charge of the products formed under more acidic conditions is greater for Fe
58 coagulants than for Al (Vilge-Ritter et al., 1999).

59

60 The theoretical relationship between charge and coagulation has been known for many years
61 and was first demonstrated experimentally for potable water treatment in the 1950s (Black
62 and Chen, 1965; Gupta et al., 1975; Packham and Sheiham, 1977). However, direct

63 correlation between the two has only been made in more recent times due to improvements in
64 instrumentation enabling rapid and regular measurements (Sharp et al., 2006). The
65 correlations demonstrate a range of zeta potential values where residual NOM and turbidity
66 are minimised and importantly identifies a threshold zeta potential value below which the
67 coagulant must operate. Adoption of zeta potential measurement in field situations is
68 becoming more common around the world for Fe and Al coagulants. For instance, in the UK
69 such measurements are used to diagnose coagulation problems and consider changes in
70 operating practice (Sharp et al., 2006) and has been widespread in the US for many years
71 through the application of streaming current devices (Dentel and Thomas, 1989).

72

73 However, there is now a strong drive for water treatment processes to be able to provide more
74 DOC removal than that which can be provided by both Fe or Al coagulants. This has
75 primarily been driven by an increase in NOM levels in source waters across the world. This
76 has continued to such an extent that at certain treatment works during periods of elevated
77 NOM flux, coagulant demand is becoming excessive and/or removal is insufficient to
78 maintain a sufficient reduction in disinfection by product (DBP) formation (Mergen et al.,
79 2008). There is also a significant problem associated with a reduction in floc strength when
80 high NOM loads enter the WTWs, resulting in poor removal in solid-liquid separation
81 processes (Jarvis et al., 2008). In such cases, current practice is to pre-treat the source water
82 to reduce the NOM load prior to coagulation with processes such as magnetic ion-exchange
83 (MIEX) (Singer and Bilyk, 2002). The MIEX process in combination with coagulation shows
84 improved removal and substantial reduction in THM formation as well as a significant
85 improvement in particle properties although concerns remain related to treatment and
86 installation costs and the suitability of the process for a range of water types.

87

88 A possible solution to both floc strength reduction and inadequate NOM removal has been
89 postulated based around the use of alternative metal ions such as zirconium (Zr) salts which
90 have been investigated for treatment of arsenic removal (Lakshmanan et al., 2008), NOM
91 (Jarvis et al., 2008) and paper and pulp effluent (Ayukawa, 1978). One reason for
92 consideration of Zr as a coagulant lie with its increased positive charge compared with Al and
93 Fe with species bearing a charge of up to 8^+ being reported. However, previous attempts to
94 find highly charged hydrolysis products have not been successful (Veyland et al., 1998).
95 Regardless, a comparative trial of alternatives to traditional coagulants involving Zr,
96 UV/H₂O₂, Fenton's reagent and MIEX+Fe coagulation showed that Zr coagulation gave the
97 largest improvement in both DOC removal and residual THM formation potential (THMFP)
98 reduction (Jarvis et al., 2008). The objectives of the current paper were therefore to provide a
99 more detailed investigation into the potential for Zr as a coagulant in both batch laboratory
100 experiments and continuous pilot scale treatment. This has been achieved by assessing its use
101 against traditional alum and ferric sulphate coagulants with respect to NOM removal and
102 particle properties. These chemicals represent, in the case of alum, the most widely used
103 coagulant across the world (Hammer and Hammer, 2007) and, in the case of ferric sulphate,
104 the most effective coagulant for enhanced NOM removal (Eikebrokk, 1999; Matilainen et al.,
105 2005).

106

107 2. MATERIALS AND METHODS

108 The NOM rich water source used in the jar tests was from a reservoir in the north of the U.K.
109 The coagulants under investigation were Ferripol XL, a ferric sulphate based coagulant
110 (Huntsman Tioxide Europe Ltd, Billingham), aluminium sulphate (Fisher Scientific UK,
111 Loughborough, UK) and a zirconium oxychloride based coagulant (Zr-Coag[®], Water
112 Innovate Ltd, Cranfield, UK). The Zr coagulant contained 20% weight equivalent ZrO₂

113 consisting of cationic hydroxylated polynuclear zirconium species. The specific gravity of the
114 coagulant was 1.34 and had a pH of <1. After validation of the coagulant performance in
115 laboratory jar tests, the scale of treatment was increased by performing tests on a pilot scale
116 water treatment facility. Due to the duration of the testing, water was taken from the same
117 water source at different points in time so it was necessary to optimise coagulation after each
118 water collection.

119

120 2.1 Jar Tests

121 Coagulation trials were undertaken on a PB-900 jar tester (Phipps and Bird, VA, USA) using
122 cylindrical jars containing 1 L of raw water. Mixing involved a 60 s rapid mix stage at 200
123 rpm followed by a 15 minute flocculation stage at 30 rpm and a 15 minute settlement period.
124 Settled water samples were analysed for turbidity (Hach 2100N turbidimeter, Manchester,
125 UK) and zeta potential (Zetasizer 2000, Malvern Instruments, Malvern, UK). Measurement
126 of zeta potential assumes sphericity of particles, so it was therefore probable that a small but
127 consistent and repeatable error was evident on the zeta potentials reported for the residual
128 floc particles for the different systems. Further analysis was performed after filtration through
129 a 0.45 µm glass microfibre filter (Fisher Scientific, Loughborough, UK). DOC was measured
130 using a TOC analyser (Shimadzu 5000A, Milton Keynes, UK). The UV₂₅₄ absorbance was
131 measured using a Jenway 6505 UV/Vis Spectrophotometer (Camlab Ltd, UK) with a 40 mm
132 quartz cell supplied by Starna Brand, UK.

133

134 Floc size and breakage experiments were performed using an identical experimental setup to
135 Jarvis et al. (2008). The jar tester was connected to the optical unit of a laser diffraction
136 particle sizer (Mastersizer 2000, Malvern Instruments, Malvern, UK) by drawing water
137 through the unit at a flow rate of 1.5 L.h⁻¹ using a peristaltic pump. In each experiment, which

138 was conducted in duplicate, the rpm of the stirrer in the jar tester was increased following the
139 initial 15 minute flocculation period. Increased stirrer speeds of: 30 (7.4 s^{-1}), 40 (11.4 s^{-1}), 50
140 (15.9 s^{-1}), 75 (29.3 s^{-1}), 100 (45.2 s^{-1}) and 200 (127.5 s^{-1}) rpm were applied for a further 15
141 minutes (average velocity gradients, calculated from the Camp equation, in brackets). Floc
142 strength was interpreted from the absolute floc size for a given shear rate and the gradient of
143 the line for the power law relationship between floc size and applied shear rate.

144

145 2.2 Pilot plant studies

146 Comparison of the best performing conventional coagulant with the Zr coagulant was then
147 carried out using a continuous pilot-scale treatment system. Source water was taken from the
148 same source as for the jar tests and transported to Cranfield University's pilot plant hall using
149 a 30 m^3 tanker and was fed directly from the tanker to the pilot plant during experimental
150 runs.

151

152 The pilot plant used in the experiments consisted of a rapid mix tank, two flocculator tanks in
153 series, dissolved air flotation (DAF) and sand filtration (Figure 1). This configuration was
154 used as it simulates a typical flowsheet used at full-scale for treating a high organic content
155 water of this type. Raw water was pumped through the plant at 200 L.h^{-1} . The flow through
156 the plant was controlled using a flow meter coupled to a valve positioned before the rapid
157 mixing tank. The flow was calibrated prior to pilot scale testing. The feed water was mixed in
158 the rapid mix stage at 200 rpm at a contact time of 2 minutes. Fresh solutions of coagulants
159 were prepared before the start of each run. NaOH solutions of 0.5 and 0.25 M concentrations
160 were prepared for pH adjustment of coagulation. The coagulant and pH adjusting chemicals
161 were pumped into the coagulation tank using peristaltic pumps. The pH was monitored with a
162 Jenway 2300 pH meter (Fisher scientific, UK) with an epoxy pH electrode (Fisher scientific,

163 UK). The coagulation pH was recorded every 5 min and adjustment was made if necessary to
164 keep the pH at the desired level. The coagulated water was then mixed at 5 rpm in the
165 flocculator tanks with a combined contact time of 24 minutes. The DAF unit consisted of a
166 saturator system, an air saturator pump and a cylindrical flotation column leading to an open
167 water tank. The surface overflow of the DAF unit was 3 m.h^{-1} and the recycle ratio was 18 %.
168 Treated water then went on to a 0.3 m diameter filter column operating at 8 m.h^{-1} , containing
169 16/30 grade sand (1-0.5 mm diameter) at a depth of 1 m. For each pilot plant experiment, the
170 plant was run in continuous operation for 6 hours. Samples were taken hourly after the DAF
171 unit and after sand filtration. Samples were measured for UV_{254} , (DOC), turbidity and zeta
172 potential as before. THMFP was measured using a modified form of USEPA Method 551.1
173 (Goslan et al., 2002). Filtered samples were chlorinated with excess chlorine and stored at 20
174 °C for 7 days in the dark. Samples were chlorinated at a dose that was five times greater than
175 the DOC concentration. Samples were buffered at pH 7 to nullify any pH effects. After 7
176 days exposure to chlorine, samples were quenched using sodium sulphite (100 mg.L^{-1}) and
177 transferred into vials containing a buffer. The buffer was 1% sodium phosphate dibasic
178 (Na_2HPO_4) and 99% potassium phosphate monobasic (KH_2PO_4) and was added to prevent
179 the transformation of other DBPs to THMs. THM4 (trichloromethane,
180 dichlorobromomethane, dibromochloromethane and tribromomethane) were analysed. The
181 total THM concentration was measured using gas chromatography (GC) with micro electron
182 capture detection (μECD) (Agilent 6890).

183

184 [Figure 1 here]

185 Figure 1: Schematic of the pilot plant.

186

187

188 3. RESULTS

189 3.1 Water characterisation and coagulation tests

190 The raw water used in the jar tests was typical of a UK moorland water source in terms of the
191 balance of DOC (12.9 mg.L^{-1}) and UV_{254} absorbance (57 m^{-1}) leading to a high specific UV
192 absorbance (SUVA) of $4.8 \text{ L.mg}^{-1}.\text{m}^{-1}$. The water was of low turbidity (3.5 NTU) and low
193 alkalinity of $<10 \text{ mg.L}^{-1}$ as CaCO_3 . Consequently, the source water was regarded as being
194 typical of the type being treated at a water treatment works (WTWs) where they are
195 considering upgrading its treatment facilities with MIEX technology to reduce load demand
196 (Singer and Bilyk, 2002; Jarvis et al., 2008).

197

198 The comparison of the three coagulants was determined for three doses that were
199 representative of the range of operational coagulant doses applied at the WTWs for removal
200 of NOM ($5, 10, 15 \text{ mg.L}^{-1}$ as M^+) representing dose ratios of 2.58, 1.29 and 0.86
201 $\text{mg}_{\text{DOC}}.\text{mg}_{\text{M}^+}^{-1}$ respectively (Figure 2). In all cases, the Zr systems generated more positive
202 zeta potentials and a higher isoelectric point (IEP) than Fe or Al, demonstrating that the Zr
203 coagulant provided more charge neutralising power than the other coagulants on a mass basis.
204 The zeta potential of the NOM-coagulant complexes switched from positive to negative
205 charge as the pH was increased. The IEP of the Zr-NOM system increased from pH 5.3 to 6.3
206 as the dose ratio decreased from 2.58 to $0.86 \text{ mg}_{\text{DOC}}.\text{mg}_{\text{Zr}}^{-1}$.

207

208 Minimum DOC residuals at a dose of 5 mg.L^{-1} were 1.3 mg.L^{-1} for Zr at a pH of 4.5; 1.9
209 mg.L^{-1} for Fe at a pH of 4.5-5 and 3 mg.L^{-1} for Al at a pH of 5. Increasing the dose decreased
210 the DOC residual for each coagulant such that at the highest coagulant dose of 15 mg.L^{-1} , the
211 DOC residual was 0.6, 1.5 and 2.4 mg.L^{-1} for Zr, Fe and Al respectively. The difference in
212 removal between Fe and Al is consistent with other reported comparative trials and can be

213 further extended to show that Zr provides additional removal of NOM above that of Fe. For
214 Zr it was apparent that the lowest residual turbidity was not seen over the same pH conditions
215 as for the lowest residual DOC (Figure 2). At 5 mg.L⁻¹, Zr gave the lowest turbidity between
216 pH 5-6 (0.25 NTU). Below pH 5, residual turbidity rapidly deteriorated. At 10 mg.L⁻¹ the
217 lowest turbidity for Zr shifted to higher pH between 6-7 (0.31-0.38 NTU). At pH <6.0,
218 residual turbidity deteriorated. At 15 mg.L⁻¹, the lowest turbidity residual was seen between
219 pH 6-8 (0.63-1.28 NTU). For the three coagulants investigated based on combined DOC
220 removal and turbidity removal, it can be seen that Zr operates over a wider range of zeta
221 potentials for optimum removal, but has more specific pH requirements than the other
222 coagulants for a given dose to reach the required zeta potential range (Table 1). The results
223 agree with previous work treating similar waters showing that as long as coagulation is
224 carried out within the correct zeta potential range, optimum particle and NOM removal will
225 be achieved (Sharp et al., 2006).

226

227 [Figure 2 here]

228 Figure 2: Performance comparison of the Zr, Fe and Al coagulants at 5-15 mg.L⁻¹.

229 Table 1. Optimum conditions for coagulation of NOM with the three coagulants.

230 [Table 1 here]

231

232 3.2 Floc properties

233 Floc characteristics were measured for coagulation conditions that represented optimised
234 treatment within the previously determined operational zeta potential windows (Table 1).
235 These were doses and pH levels of 5 mg.L⁻¹ at pH 5.5 (-1 mV) for Zr; 8 mg.L⁻¹ at a pH of 4.5
236 (-3 mV) for Fe; 10 mg.L⁻¹ at a pH of 6 (-4 mV) for Al. Comparison of the floc size was made
237 using the median equivalent volumetric diameter (d₅₀). Analysis of the floc growth profiles

238 showed significant differences for the average steady state d_{50} floc sizes for the three different
239 coagulants across the 7 duplicated runs (Figure 3). In the case of Zr flocs, the d_{50} floc size
240 ranged between 870-990 μm with an average of 930 μm . In contrast, Fe flocs were
241 considerably smaller with a range of 670-790 μm and an average of 710 μm and Al flocs
242 were smaller still with a range between 430-490 μm and an average of 450 μm . In
243 comparison, application of a pre-treatment with MIEX resin followed by Fe coagulation
244 (MIEX+Fe) on water from the same source water during a different trial yielded large flocs
245 with a median size of 1020 μm (Jarvis et al., 2008) indicating that Zr flocs approach those
246 obtained when using pre-treatment. The three systems also showed differences in growth
247 profiles with the growth rates being fastest for the Al flocs at around 520 $\mu\text{m}\cdot\text{min}^{-1}$ compared
248 to 220 $\mu\text{m}\cdot\text{min}^{-1}$ for Zr and 190 $\mu\text{m}\cdot\text{min}^{-1}$ for the Fe flocs. After a spike in floc size, the fast
249 growing Al flocs reached a steady state size after 3 minutes, whilst it took 4 minutes for the
250 Zr flocs and 5 minutes for the Fe flocs.

251

252 Once the flocs had reached a steady state size during the slow stir phase, they were exposed
253 to increased shear rates. The breakage pattern for the Fe and Al flocs followed a classical
254 response composed of two components: at elevated shear levels above 75 rpm ($G_{av} = 29.3 \text{ s}^{-1}$)
255 a rapid decrease in floc size was observed within the first minute after the increased shear rate
256 had been introduced followed by a more gradual change in floc size (Figure 3d). This was
257 ascribed to a fragmentation breakage mechanism causing a large change in floc size
258 distributions followed by an erosion breakage mechanism as small particles erode from the
259 parent floc. Below 75 rpm only a gradual decline in floc size occurred as the shear conditions
260 erode the flocs rather than cause large-scale fragmentation. To illustrate, in the case of Fe,
261 upon exposure to an elevated shear rate of 50 rpm (15.9 s^{-1}) the median floc size initially
262 decreased from 680 to 620 μm ; whereas at 75 rpm (29.3 s^{-1}) the median floc decreased from

263 730 to 550 μm and at 200 rpm (127.5 s^{-1}) from 755 to 397 μm . Thereafter the floc size
264 decreased in an approximate power law relationship, reaching final median sizes of 535, 389
265 and 245 μm respectively. In contrast, the Zr floc system did not exhibit such an initial rapid
266 decrease in floc size upon exposure to any level of elevated shear. Instead, the median floc
267 size decayed with a power law coefficient of -0.51, -0.90, -2.49 at elevated shear rates of 50,
268 75 and 200 rpm respectively. No difference could be observed between the breakage profiles
269 at 150 rpm (86.2 s^{-1}) and 200 rpm (127.5 s^{-1}) indicating that the flocs had reached a stable
270 response against exposure to elevated shear rate beyond 150 rpm (86.2 s^{-1}).

271

272 Overall comparison of the strength of the flocs through a plot of final steady state size against
273 shear rate (Figure 3d) indicated that whilst the Zr flocs were initially larger, all three systems
274 approached a similar median floc size of 245-277 μm at very high levels of elevated shear
275 rate (200 rpm, 127.5 s^{-1}). The strength of the flocs can be described in two ways from the
276 figure. The initially higher size of flocs formed during the initial slow stir phases indicates a
277 clear sequences of floc strength as $\text{Zr} > \text{Fe} > \text{Al}$. This is because larger flocs grown at any given
278 shear rate indicate a greater resistance to breakage (Yukselen and Gregory, 2004). The
279 gradient of the log-log plot, defined as the stable floc size exponent (γ), can be used to define
280 the relative strength of the floc to exposure across the whole elevated shear spectrum.
281 Observed gradients of -0.69, -0.53 and -0.29 for the Zr, Fe and Al systems indicated a clear
282 difference, with Zr and Fe more affected by exposure to elevated shear rate. The MIEX+Fe
283 line shown in Figure 3d had a gradient of -0.54, indicating that these flocs were more
284 resistant to breakage than for the Zr coagulant.

285

286

287

288 3.3 Pilot plant studies

289 The improved performance of Zr in laboratory tests was then assessed in a continuous pilot
290 plant environment. Tests were carried out using the best performing conventional coagulant
291 (ferric sulphate) in comparison with the Zr coagulant. This also enabled a direct link to be
292 made between floc properties as measured from the mixing experienced in a jar tester to the
293 removal of the flocs in flotation and filtration clarification processes.

294

295 As the water used in these trials was collected at a different point in time to the bench scale
296 jar testing experiments, it was necessary to carry out separate preliminary jar tests to establish
297 optimum dosing conditions for the new water. The water DOC and UV_{254} were 8.7 mg.L^{-1}
298 and 45.1 m^{-1} respectively. Coagulant doses of 9 mg.L^{-1} at pH 4.5 were established for
299 optimum DOC removal for both Fe and Zr coagulants based on these tests. Coagulation zeta
300 potentials were well within the optimum operational ranges for charge minimisation of NOM
301 for both coagulants (-7 mV for Fe and $+2.5 \text{ mV}$ for Zr). As seen in the jar tests, comparison
302 of direct Fe and Zr dosing showed there to be a significant difference in the removal of NOM
303 and the operation of the plant which was in close agreement with the bench scale testing
304 (Figures 4 and 5). Residual DOC (Figure 4) and turbidity (Figure 5) were found to be
305 significantly lower for Zr in comparison to the Fe coagulant (Mann-Whitney U-Test, P
306 <0.05). After flotation, DOC removal was 80.5 % after treatment with Fe (residual DOC of
307 $1.7 \pm 0.3 \text{ mg.L}^{-1}$) and 86.2% using Zr (residual DOC of $1.2 \pm 0.1 \text{ mg.L}^{-1}$). The improved
308 DOC removal when using Zr also resulted in a lower THM-FP for the final treated water. The
309 THM-FP of water sampled after the filter was $163.1 \pm 36.7 \text{ } \mu\text{g.L}^{-1}$ after treatment with Fe and
310 $100.7 \pm 15.0 \text{ } \mu\text{g.L}^{-1}$ after treatment with Zr. The amount of THMs formed per mg DOC was
311 $75.6 \pm 5.5 \text{ } \mu\text{g.mg}^{-1}$ and $68.2 \pm 8.2 \text{ } \mu\text{g.mg}^{-1}$ for Fe and Zr respectively, indicating no
312 preferential removal of DBP forming organic compounds by either coagulant.

313 The resultant removal of floc in the clarification stages matched the observations seen in the
314 laboratory experiments, with the larger and more robust Zr flocs being better removed in
315 clarification stages. The residual turbidity values observed were somewhat higher than those
316 typically seen on a full-scale water treatment facility. This was thought to be as a result of
317 scaling difficulties resulting in less effective DAF performance than when compared to a full
318 scale plant. The optimum reaction zone for bubble attachment to particles was difficult to
319 achieve using a single nozzle in the pilot plant when compared with how multiple numbers of
320 nozzles operate in a full scale system. This resulted in high particle loads onto the filters.
321 Nevertheless, as the conditions used were constant, the results obtained were very useful for
322 comparing the performance of the Zr and Fe coagulants. Following flotation, residual
323 turbidity was 6.4 ± 4.8 NTU after treatment with Fe while Zr treatment resulted in a lower
324 turbidity of 2.3 ± 0.3 NTU. After filtration, the results matched the observations seen
325 following DAF, with the Zr coagulant resulting in significantly improved residual turbidity:
326 1.2 ± 0.5 NTU for Fe and 0.4 ± 0.1 NTU for Zr (Mann-Whitney U-Test, $P < 0.05$).

327

328 [Figure 3 here]

329 Figure 3: Comparison of floc strength of Zr, Ferric and Alum flocs.

330

331 [Figure 4 here]

332 Figure 4: Residual DOC measured after DAF and after the filter during pilot plant treatment
333 with Fe and Zr coagulants under optimum conditions (the bars represent the maximum and
334 the minimum values, the box the 25th to 75th percentile values and the data point the mean).

335

336 [Figure 5 here]

337 Figure 5: Turbidity measured after DAF and after the filter during pilot plant treatment with
338 Fe and Zr coagulants under optimum conditions (the bars represent the maximum and the
339 minimum values, the box the 25th to 75th percentile values and the data point the mean).

340

341 4. DISCUSSION

342 The results presented in this work show a definite improvement in performance when using a
343 Zr based coagulant for the treatment of NOM compared to the more traditional Fe and Al
344 salts at both laboratory and pilot scale. When optimised for combined DOC removal and low
345 residual turbidity, Zr out-performed the other coagulants tested. Improvements were
346 demonstrated in terms of the achievable residual, lower THMs and the floc properties
347 formed. Analysis of the jar testing data indicated that the best conditions for coagulation of
348 NOM using Zr was between pH 5-6 for doses of between 5-15 mg.L⁻¹. Below this pH, floc
349 properties rapidly deteriorated which was coincidental with an increased residual turbidity
350 and an increase in the positive charge of the system. These data indicate that particle re-
351 destabilisation occurs as a result of the high positive charge added by the Zr coagulant
352 compared with the Fe and Al coagulant. The consequence of which is the necessity for
353 careful control of coagulation conditions when using Zr to ensure the successful operation of
354 solid-liquid separation processes at full scale WTWs.

355

356 For Fe and Al coagulants, dose minimisation occurs under acidic conditions as more highly
357 charged hydrolysis species exist enhancing the neutralising power of the coagulant. The
358 improved NOM removal performance for Zr over conventional coagulants was comparable to
359 that seen for treatment systems that utilise MIEX+Fe (Singer and Bilyck, 2002) whilst also
360 producing similar quality flocs in terms of physical characteristics (Jarvis et al., 2008).
361 Consequently, the practical significance of using Zr coagulation is as a direct replacement for

362 Fe or Al in instances where additional NOM removal is required and may negate expensive
363 installation of new treatment technology such as AOPs or ion-exchange systems. The
364 explanation for the improved NOM removal by Zr is not easily elucidated from these results
365 or from the literature. Some authors have proposed very highly charged cationic hydrolysis
366 species being formed when Zr is dissolved in water, such as $[\text{Zr}_3(\text{OH})_3]^{8+}$ (Baes and Mesmer,
367 1976). Other workers have identified $[\text{Zr}(\text{OH})(\text{OH}_2)_7]^{3+}$ and a cyclical tetramer of
368 $[\text{Zr}_4(\text{OH})_8(\text{OH}_2)_{16}]^{8+}$ (Rose et al, 2003). However, other authors have only found species with
369 a +1 charge (Veyland et al, 2008). Whilst the distribution of hydrolysis products remains
370 unclear, the higher zeta potential and IEP for the Zr coagulant demonstrates that it provides
371 more charge than the alternative coagulants. The improvements may therefore relate to
372 increased charge on precipitated Zr solids, which have been demonstrated to be important for
373 alum coagulants (Letterman and Iyer, 1985; Dentel 1988).

374

375 The observation that the Zr coagulant had a much narrower pH range of operation when
376 compared with the Fe and Al coagulants may be linked to the ion associated with the metal
377 coagulant. Sulphate has been shown to be a strongly adsorbing anion which can destabilise
378 systems in which coagulant has been overdosed, effectively extending the operational pH
379 range over which the coagulant may operate (Letterman and Vanderbrook, 1983).
380 Oxochloride is a less well adsorbed ion and therefore does not produce the same effect,
381 further indicating that more precise control of the Zr coagulant's operational range is
382 required.

383

384 The parameter of floc strength is difficult to both define and measure leading to a number of
385 approaches. However, irrespective of approach, it is accepted that the strength of the
386 aggregate relates to the combination of the number and strength of the bonds formed (Bache,

387 2004). In the analysis performed here, it was shown that Zr flocs formed under optimised
388 conditions for combined NOM removal and residual turbidity were larger and better removed
389 than for the conventional coagulants for laboratory and pilot scale systems. In pilot plant
390 experiments, it was demonstrated that the flocs formed by the Zr coagulant were better
391 removed in flotation and filtration processes meaning that solids loading onto filters was
392 reduced with the potential for offering longer filter run times. The reasons for this improved
393 removal in DAF and filtration are two-fold: 1) as a result of the increased strength of Zr flocs
394 and 2) increased electrostatic attraction between bubbles and floc for Zr systems. Given that
395 bubbles are negatively charged in DAF applications (Dockko and Han, 2004), the more
396 positively charged Zr flocs will have a strong affinity for the oppositely charged bubbles,
397 improving the overall floc removal.

398

399 Whilst the Zr-NOM floc size was most affected by changing rpm, the median floc size was
400 able to remain larger than that of the other coagulants throughout, indicating that the Zr flocs
401 had greater inherent strength than for the flocs formed from the other coagulants. The
402 increased breakage of the larger flocs was expected as they are exposed to micro-scale energy
403 dissipating eddies which smaller flocs can get entrained into rather than being broken by
404 (Boller and Blaser, 2004). Overall the strength of the connection points in a floc is based on a
405 force balance including steric, van der Waals, polymer bridging and electrostatic forces
406 (Gregory, 1989). Zeta potential provides a suitable means of considering the role of
407 electrostatic effects and provides the most convenient way to control floc properties in
408 practice (Sharp et al., 2006), such that when these forces are minimised floc strength is
409 maximised. The current work continues this development with the identification of a zeta
410 potential window of -10 to +10 mV for the Zr coagulant, compared with -8 to +5mV for Fe
411 and -8 to 0 mV for Al for combined NOM removal and strong floc properties. A final

412 consideration for the application of a Zr based coagulant in drinking water treatment is its
413 toxicity. Zirconium is generally thought to be nontoxic as an element or in its compounds and
414 exists mostly in a physiologically inert dioxide form at pH levels associated with biological
415 activity (Blumenthal, 1976; Kroschwitz and Howe-Grant, 1999). Zirconium has hence not
416 shown any potential to be harmful to humans, but this still needs to be verified in future
417 work.

418

419 5. CONCLUSIONS

- 420 • The results from this work have established that Zr offers improved NOM removal
421 over that of conventional coagulants when using conditions optimised for DOC
422 removal and strong floc properties.
- 423 • The improved removal of NOM using Zr also resulted in lower THM formation,
424 however there was not a preferential removal of organic compounds with a high DBP-
425 FP, as reflected by the similar normalised THM-FP results.
- 426 • The Zr coagulant requires careful control of the coagulation conditions before charge
427 reversal and re-stabilisation is observed causing a poor quality floc to be formed.
- 428 • The Zr coagulant produced strong, robust flocs which showed better clarification than
429 conventional coagulants in sedimentation systems (jar tests) and flotation processes
430 (pilot scale) when coagulation conditions had been selected for optimised NOM and
431 turbidity removal.

432

433

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