

1 **Removal of metals from mine drainage waters by in situ mineral sorbent-based**
2 **pilot filter systems**

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17
18 **Abstract:**

19 Discharge of metal-containing wastewater streams into the environment is an environmental concern
20 because these pollutants do not degrade and tend to bioaccumulate. A number of laboratory-based
21 investigations on the effectiveness of a wide range of filter materials for metal removal from diluted
22 wastewater streams have been reported. However, only a few pilot or full-scale investigations have
23 been conducted. Therefore, this study investigated the metal retention capabilities of mineral-based
24 filter materials (commercially available mineral product (5-15 mm), recycled mineral material (2-4

25 mm) and slag by-product (2-4 and 4-16 mm)) when used in pilot-scale filter systems under continuous
26 operation in a closed mining area in North Ostrobothnia, Finland, between June and October 2017.
27 The influence of material particle size on system function and on metal retention efficiency was also
28 evaluated. The results revealed that system performance was dependent on material composition and
29 particle size (smaller particle size being more effective). The highest metal removal efficiencies (Zn,
30 Ni, Cd, Cu and Pb) and largest amount of water treated (per volume of material applied) were
31 achieved by an aluminium oxide-based recycled mineral material (2-4 mm). While smaller-grained
32 materials performed better in terms of removal efficiency, the removal rates achieved by coarser-
33 grained, commercially available mineral product (5-15 mm) were comparable to those achieved by
34 small-grained slag (2-4 mm). Full-scale systems using the recycled mineral product (2-4 mm) would
35 have an approximately two-fold longer material replacement time than systems using the slag (2-4
36 mm). Replacement time for the larger-grained materials tested could not be determined, due to
37 problems with freezing. Overall, the recycled mineral material tested can be recommended for full-
38 scale tests, especially when high zinc removal rates are required.

39

40 **Keywords:** Purification efficiency, mining waters, slag, recycled mineral, sorption

41

42 **Highlights:**

- 43 - In situ pilot-scale tests enabled good evaluation of filter materials
- 44 - Smaller-grained materials were more effective in metal removal
- 45 - An aluminium oxide-based recycled mineral filter achieved best metal removal

46

47 **1. Introduction**

48 Release of metals contained in e.g. mining-influenced waters (The Coal Authority, 2014), urban
49 runoff (Valtanen et al., 2014; Westerlund et al., 2003) etc. can impair surface water quality and the

50 general health of the receiving aquatic ecosystem, as these pollutants do not degrade and tend to
51 bioaccumulate in the environment (Simate and Ndlovu, 2014). As regards mining-influenced waters,
52 concentrations of metals can vary depending on the type of mine and on where the water originates
53 from inside the mine site (drainage, process etc.) (Akcil and Koldas, 2006; Palmer et al., 2015). Any
54 water treatment system aimed at reducing metal load into the environment must therefore cope with
55 water quality variations. At operational mining sites with highly polluted waters (e.g. mining process
56 waters), active purification methods for metal removal, such as chemical precipitation, distillation,
57 evaporation, electrolysis and activated carbon, are employed (Fu and Wang, 2011; The Coal
58 Authority, 2014). Passive methods such as wetlands, filters and bio-filters can be applied for removal
59 of metals from diluted streams such as mining area drainage water and for pollution control at closed
60 mining sites (Clar et al., 2004; Fu and Wang, 2011). The suitability of passive methods depend on
61 different factors such as location, available space, and amount and quality of water to be treated. For
62 example, if available space is the limiting factor and water amount is not too large (drainage area
63 maximum 0.8-4 ha; Clar et al., 2004), a filter-type system can be a feasible alternative. When planning
64 a filter-type system, important factors to be taken into consideration are the quality of the inflow
65 water, and the particle size and composition of the filter material. The effectivity of different materials
66 depend on the type and concentration of metals contained in the water (Clark et al., 2005) as ions
67 compete for sorption sites. The pH of the water affects the surface charge of materials and the
68 speciation of metals, thus affecting sorption efficiency. Particle size influences bulk porosity and the
69 risk of clogging, with finer-grained materials being more susceptible to clogging than coarser-grained
70 materials (Vohla et al., 2011). On the other hand, finer-grained materials provide a larger surface area
71 (higher number of sorption sites), which increases the capability of the filter medium to retain metal
72 ions (Chuah et al., 2005). Moreover, high metal content in the material can cause leaching (Lim et al.,
73 2015) and increased concentrations in outflow water.

75 A number of laboratory-based investigations into the effectiveness of a wide range of filter materials
76 for metal removal from wastewater streams have been reported (e.g. Genç-Fuhrman et al., 2007;
77 Gogoi et al., 2018; Hatt et al., 2008; Lim et al., 2015; Reddy et al., 2014). However, reports on pilot-
78 scale or full-scale tests are scarce (Assmuth, 2017; Clark et al., 2005). While laboratory-scale
79 experiments are important and provide the opportunity to investigate processes and mechanisms in
80 more detail, pilot- and full-scale tests are needed to fully assess the suitability of materials and systems
81 (Hatt et al., 2008). Such tests should submit materials and systems to the challenges faced in real-life
82 applications, such as variations in water quality, temperature and/or volume.

83

84 Based on the identified need for pilot- or full-scale experiments, the aim of this study was to assess
85 the metal retention capabilities of different mineral-based filter materials (commercially available
86 mineral product, recycled mineral material and slag by-product) when used in filter-type pilot-scale
87 systems. Tests were carried out in a closed mine site (Northern Finland) and real mine area drainage
88 water was used. The influence of filter material type and particle size on the system's function and
89 metal retention efficiency were evaluated.

90

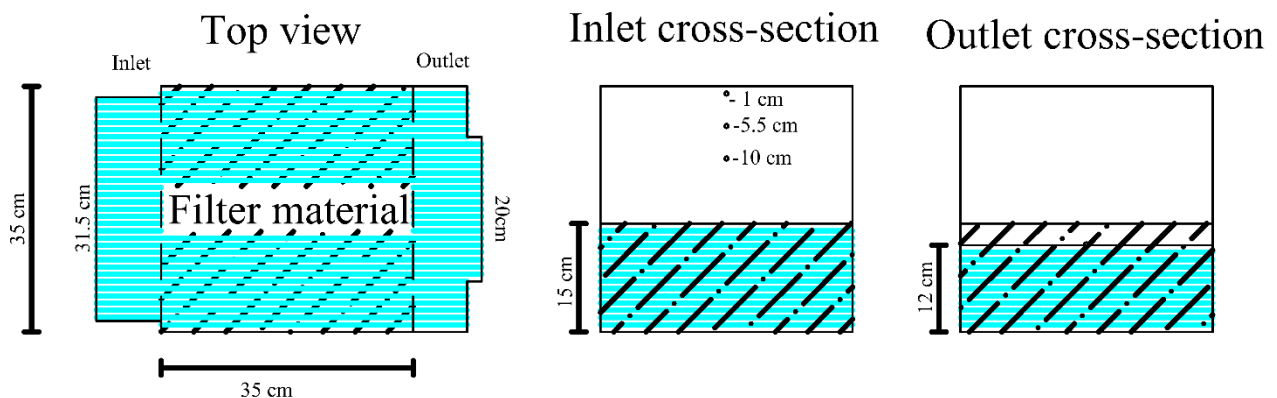
91 **2. Material and methods**

92 *2.1 Pilot design and operation*

93 Filter pilot systems were tested in a closed mining area in North Ostrobothnia, Finland, from mid-
94 June to late October, 2017. Inflow water for the systems was pumped from a ditch carrying leachate
95 from an old mine tailing area. The study was conducted as part of the HuJa (ERDF) project.
96 “Enhancing the treatment of metal-containing storm-waters and wastewaters using natural materials”.
97 Material selection was based on preliminary laboratory-based studies (Gogoi et al., 2018 and
98 unpublished data) and suggestions from project collaborators. Important factors taken into
99 consideration were metal retention capacity (especially for Zn), high hydraulic conductivity and

100 material grain size. Selected materials were: recycled mineral product ALOXrc (2-4 mm; referred to
101 as Mineral R) and commercial available mineral sorbent product PalPower M10 (5-15 mm; referred
102 to as Mineral P) from Aquaminerals Finland Oy, OKTO JT-sand (2-4 mm) and OKTO chippings (4-
103 16 mm) by-product slags from ferrochrome production by Outokumpu Chrome Oy (referred to as
104 Slag).

105
106 The pilot systems consisted of plastic boxes (about 55 cm x 35 cm x 30 cm), where compartments
107 were created (inlet, filter media and outlet) using perforated plastic walls (holes 5 mm, located 2.5-3
108 cm apart) and 1 mm plastic netting. The adsorbent materials were placed in the compartments in a
109 layer measuring around 35 cm x 35 cm x 15 cm (Fig. 1). Slots for inlet pipe (inner diameter 4 mm)
110 connection were installed at three different depths (-1, -5.5 and -10 cm from the top). This was done
111 to overcome any variation in pressure head during the tests, so that flow velocity could be kept as
112 stable as possible. The outlet pipe (inner diameter 6-8 mm) was placed at 12 cm from the bottom of
113 the unit and was fitted with a 1 mm plastic net at the entrance to prevent blocking of the pipe with
114 leaves and other materials transported with the water. The pilot systems (boxes) were covered to
115 prevent the entry of foreign material.



116
117 Fig. 1. Top view of the pilot-scale filter system and cross-section of the inlet and outlet.

118

119 Pilot operations started in mid-June 2017 with two filter boxes filled with the finer-grained (2-4 mm)
 120 Slag and Mineral R materials (Table 1). In August, clogging of the system using the Slag material
 121 was observed, so the material in the box was changed to a larger-grained Slag material (4-16 mm)
 122 and a third filter box was established and filled with larger-grained Mineral P material (5-15 mm).
 123 The desired water residence time in the systems was about 30 minutes, which would be a suitable
 124 scaling up parameter for filters to be constructed in the existing ditches. Volumetric inflow rate to
 125 each pilot was set as accurately as possible based on the three inlet depths (-1, -5.5 and -10 cm from
 126 the top of box) to meet the desired residence time.

127

128 Table 1. Information on operation of the different filter units, amounts of material tested, test period
 129 and reason for test interruption.

Material	Amount of material (kg) (m ³)		Test period ^a	Test time (d)	Reason for ending the test
Mineral R (2-4 mm)	18.60	0.018	13.6- 11.10.17	120	Clogging
Slag (2-4 mm)	29.74	0.019	13.6- 16.8.17	64	Clogging
Mineral P (5-15 mm)	20.79	0.018	16.8- 11.10.17	49	Freezing 23.10.17
Slag (4-16 mm)	31.27	0.019	16.8- 11.10.17	49	Freezing 23.10.17

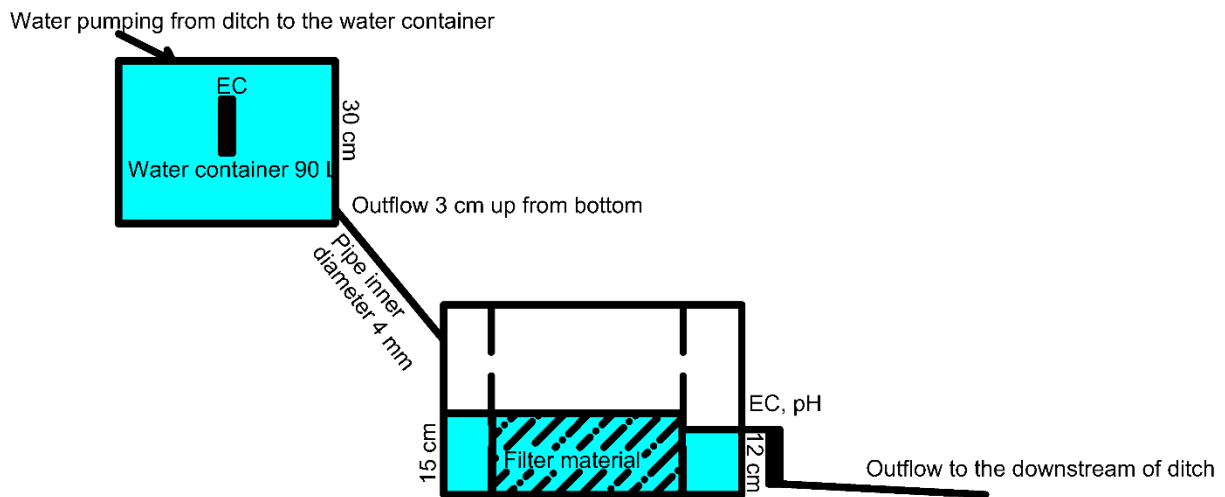
130 ^aThe coarser material units operated until 23.10.17 (61 days), but the water amount and water quality data were only
 131 recorded until 11.10.2017. Therefore, only collected data was used in calculation of treated water volume.

132

133 During the tests, water was pumped from the ditch to a 90-L container by one (operation with two
 134 pilot filter units) or two (operation with three pilot units) pumps (Biltema: model 25-2751; Fig. 2).
 135 The water storage container was filled by intermittent activation of the pumps, controlled by ON/OFF
 136 timers. The storage tank was filled every 90 min during operation with one pump and every 45 min
 137 during operation with two pumps. From the 90-L water container, the water travelled by gravity via
 138 the inlet pipe to the filter pilot inlet compartment. Gravity was also the driving force behind the flow
 139 of water through the filter material (around 0.5-1.5% longitudinal slope) to the outlet area and from

140 there to the outlet pipe. The outlet pipe discharged to a small container, where electric conductivity
141 (EC) and pH were measured. From the small container, the water discharged to the same ditch
142 downstream of the pump extraction point (see Fig. 2).

143



144

145 Fig. 2. The pilot filter system and water flow routes.

146

147 2.2 Monitoring

148 The EC measurements were carried out continuously (frequency 15 min) by HOBO-loggers installed
149 at the water storage tank and at the outflow of the pilot systems to monitor changes in the ionic
150 strength of the water. In addition, manual pH and EC measurements (WTW Multi 350i-meter) were
151 made and water samples were taken at the same points during field visits, which were made every
152 day or every second day at the start of the test and every 2 weeks for the rest of the operating period.

153 Inflow and outflow samples were taken from the 90-L water container and outlet pipe, respectively.

154 Monitoring of water flow conditions and maintenance work such as unblocking and cleaning pipes
155 etc. were carried out during site visits.

156

157 Due to the intermittent pumping, the water level inside the water storage container varied, which
158 caused flow velocity variations in the pilot systems. For that reason, inflow rate was determined on

159 a few occasions by collecting the water discharging from inlet pipes. Water was collected at different
160 times, i.e. different water pressure levels inside the same pumping cycle, into a volumetric container
161 for a specific amount of time (e.g. 3 min). The average inflow rate was determined from the measured
162 values, taking into consideration how water level varied in the storage tank due to pumping regime.
163 Outside those occasions, if disturbed flow conditions were noted in a specific pilot, e.g. due to
164 clogging problems in pipes, inflow rates were estimated based on the water level in the 90-L water
165 container relative to the pumping cycle (e.g. how much water was in the container just before each
166 new pumping cycle).

167

168 *2.3 Analytical and other determination methods*

169 During the test period, inflow water samples were collected on 13 different occasions and on five of
170 these occasions, a portion of the water collected was filtered (glass fibre (GF) 0.45 µm syringe filter).
171 From the outflow of units containing Mineral R (2-4 mm), Slag (2-4 mm), Mineral P (5-15 mm) and
172 Slag (4-16 mm), the number of samples (unfiltered/filtered) taken was 13/5, 8/2, 6/3 and 6/3,
173 respectively. Filtered and unfiltered samples (acidified as pre-treatment) were sent for elemental
174 analysis to an accredited laboratory. Elements analysed (SFS-EN ISO 11885:2009) using ICP-OES
175 method were Ca, K, Mg, Na and Si. Elements analysed (SFS-EN ISO 17294-2:2016) using ICP-MS
176 method were Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, U, V and
177 Zn. When total concentrations (unfiltered samples) were analysed (SFS-EN ISO 17294-2:2016), the
178 ICP-MS method was used for Cd, Ni, Cu, Cr, Zn, As and Pb. Note that, the total concentrations were
179 determined significantly more often than the dissolved concentrations of different metals. Thus, it
180 was not possible to establish a direct correlation between the average dissolved and total
181 concentrations determined.

182

183 On two occasions, inflow samples were also analysed for: total nitrogen (Tot.N, SFS-EN ISO 11905-
184 1), sum of nitrate and nitrite nitrogen (NO₂₊₃-N, SFS-EN ISO 13395), ammonia nitrogen (NH₄-N,
185 Sis. A56 Skalar analytical method no.158.), dissolved organic carbon (DOC, Sartorius Minisart®
186 0,45µm membrane filter, SFS-EN 1484), total phosphorus (Tot.P, SFS-EN ISO 15681-2, CFA-
187 technics), phosphate phosphorus (PO₄-P, SFS-EN ISO 15681-2, CFA-technics) and chloride (Cl,
188 SFS-EN ISO 10304-1), and, on one occasion, sulphate (SO₄, SFS-EN ISO 10304-1). The
189 determination accuracy and detection limit of the methods used are presented in Table S1
190 (Supplementary material). In the calculations performed, values under the detection limit were
191 assumed to be 80% of the limit. Variation in inflow water (elements or compounds) concentrations
192 was presented as standard deviation (s_d) if n>2.

193

194 Average inflow rate and inflow and outflow concentrations for two consecutive field visits were used
195 as the inflow or outflow value of that period. Outflow rates were assumed to be equal to inflow rates,
196 due to the small size of the system, and thus no significant effect of e.g. evaporation should have
197 occurred. Inflow and outflow pollutant load was calculated based on average discharge rates and the
198 average inflow and outflow concentrations between two consecutive sampling times. Load was
199 calculated as the sum of average inflow rates and concentrations between two consecutive sampling
200 times and load removal as the difference between the sum of inflow and outflow load. Removal
201 efficiency, RE (%), was calculated based on the difference between load entering the system (L_{in},
202 mg) and load leaving the system (L_{out}, mg) in the whole test period:

203

$$204 \quad RE = \frac{L_{in} - L_{out}}{L_{in}} * 100\% \quad (1)$$

205

206 The minimum and maximum values and standard deviation (if n>2) for removal efficiencies
207 calculated for each sampling period are presented. The non-parametric Kruskal-Wallis test was used

208 to evaluate if the difference in removal efficiency values distribution obtained from pilot systems
209 using different filter media was statistically significant ($p < 0.05$). The test was performed using SPSS
210 statistical software.

211

212 Water residence time was determined at the start and end of pilot system operation. At the start of the
213 tests, the residence time (t_r , min) and porosity of filter media (Φ) was determined based on equations
214 2 and 3.

$$215 \quad t_r = \frac{V_s * \Phi}{Q_{in}} \quad (2)$$

216

$$217 \quad \Phi = \frac{((t_{in} - t_{out}) * Q_{in}) - V_w}{V_s} \quad (3)$$

218

219 where:

220 V_s = volume of filter media (ml) at 12 cm height (outflow point)

221 Q_{in} = inflow (ml/min)

222 t_{in} = time (min) when water started flowing into filter system

223 t_{out} = time (min) when water started to discharge from filter system

224 V_w = volume of water (ml) in the inlet and outlet compartments (water filled) of filter systems at 12
225 cm height (outflow point).

226

227 At the end of the tests, the system residence time was determined by a conservative tracer experiment
228 in which sodium chloride (NaCl; 3.5 g in 0.5 L; feed in 1-2 min pulse) was used as tracer and changes
229 in the electric conductivity of outflowing water were monitored. A detailed description of
230 determination of mean residence time using the conservative tracer method can be found in Postila et
231 al. (2015). The residence time in the filter compartment was calculated by subtracting the water
232 residence time in the inflow and outflow compartments from the system's residence time determined.

233 Due to low temperatures, some of the water inside filters containing the coarser-grained materials
234 was found to be frozen on the last site visit. The pilot systems were then transported to university
235 laboratory facilities and tracer experiments were conducted after complete thawing was observed. A
236 water sample for that tracer experiment was collected from the feeding ditch. Before tracer
237 experiments were carried out, a small sample of the filter materials was removed for characterisation
238 analysis.

239

240 Elemental composition of fresh material and spent material (collected after pilot experiments, before
241 tracer tests) was analysed (one fresh and one spent material sample per product taken close to inlet
242 area of pilots). Materials were first crushed to about 2 mm grain size (>80% <2 mm and <20% >2
243 mm) with a Rocklabs Boyd Crusher and then crushed samples (containing both fractions) were
244 pulverised to <75 µm size (>95%) with an Essa LM2 mill. The pulverised samples (containing both
245 fractions) were then mixed with a flux of lithium metaborate and lithium tetraborate and fused in an
246 induction furnace (1050 °C, ~3 min). The molten melt was immediately poured into a solution of 5%
247 nitric acid containing an internal standard, and mixed continuously until completely dissolved (~30
248 minutes). The samples were analysed for major oxides and trace elements by inductively coupled
249 plasma optical emission spectrometry (ICP-OES; Varian Vista 735 ICP) and inductively coupled
250 plasma mass spectrometry (ICP-MS; Perkin Elmer Sciex ELAN 9000). For major oxides,
251 determination accuracy is within 5% above 100x detection limit, while for minor and trace elements
252 it is within 10% above 100x detection limit. X-ray diffraction analysis of fresh and crushed materials
253 was performed using a Panalytical X'Pert Pro diffractometer equipped with a Cu X-ray source and
254 an X'Celerator detector. The XRD patterns were recorded in the 2θ range of 5-70° with a step size of
255 0.017°. The amount of metals retained (m_{ret} , mg) in the filter media material was calculated based on
256 equation 4 (based in one sample of fresh and spent material of each sorbent):

257
$$m_{ret} = c_{out} * m - c_{in} * m \quad (4)$$

258 where:

259 c_{out} = metal concentration (ppm) in spent material. If value under detection limit, it was assumed to
260 be 80% of the limit.

261 c_{in} = metal concentration (ppm) in fresh material. If value under detection limit, it was assumed to be
262 80% of the limit.

263 m = mass of material in pilot (kg)

264

265 3. Results

266 3.1 Treated water amount, residence time and field measurements (pH, EC)

267 Interruption of tests due to clogging of the system occurred only for the materials with small particle
268 size (Table 1). The amount of water treated by the Mineral R material was significantly larger than
269 that treated by the Slag (smaller particle size) product (Table 2). Measured water residence time was
270 lowest in the Slag (2-4 mm) and Mineral P (5-15 mm) pilots and highest in the Mineral R (2-4 mm)
271 pilot at the start and end of the test period. Measured water residence times were more than two-fold
272 longer at the end of the tests than at the start in all filter systems.

273

274 Table 2. Information on operation of the different filter units, porosity, residence time, discharge rate
275 and treated water volume

Material	Test duration (d)	Porosity	Residence time		Discharge av. (L/d)	Treated volume (m ³)	Treated volume/ material volume (m ³ /m ³)	Treated volume/ mass of material (m ³ /t)
			start (min)	after (min)				
Mineral R (2-4 mm)	120	0.81	31	83 ^b	425	51	2785	2743
Slag (2-4 mm)	64	0.49	19	51 ^b	406	26	1403	874
Mineral P (5-15 mm)	49 ^a	0.45	20	46 ^c	469	23	1304	1106
Slag (4-16 mm)	49 ^a	0.78	26	74 ^c	592	29	1518	927

276 ^aThe coarser material units operated until 23.10.17 (61 days), but the water amount and water quality
277 data were only recorded until 11.10.2017 (49 days).

278 ^bThe tracer test was interrupted before the electric conductivity values returned to the levels observed
279 at the beginning of the test. Therefore, the determined residence times cannot be considered accurate,
280 but they can give good estimation/indication of real values.

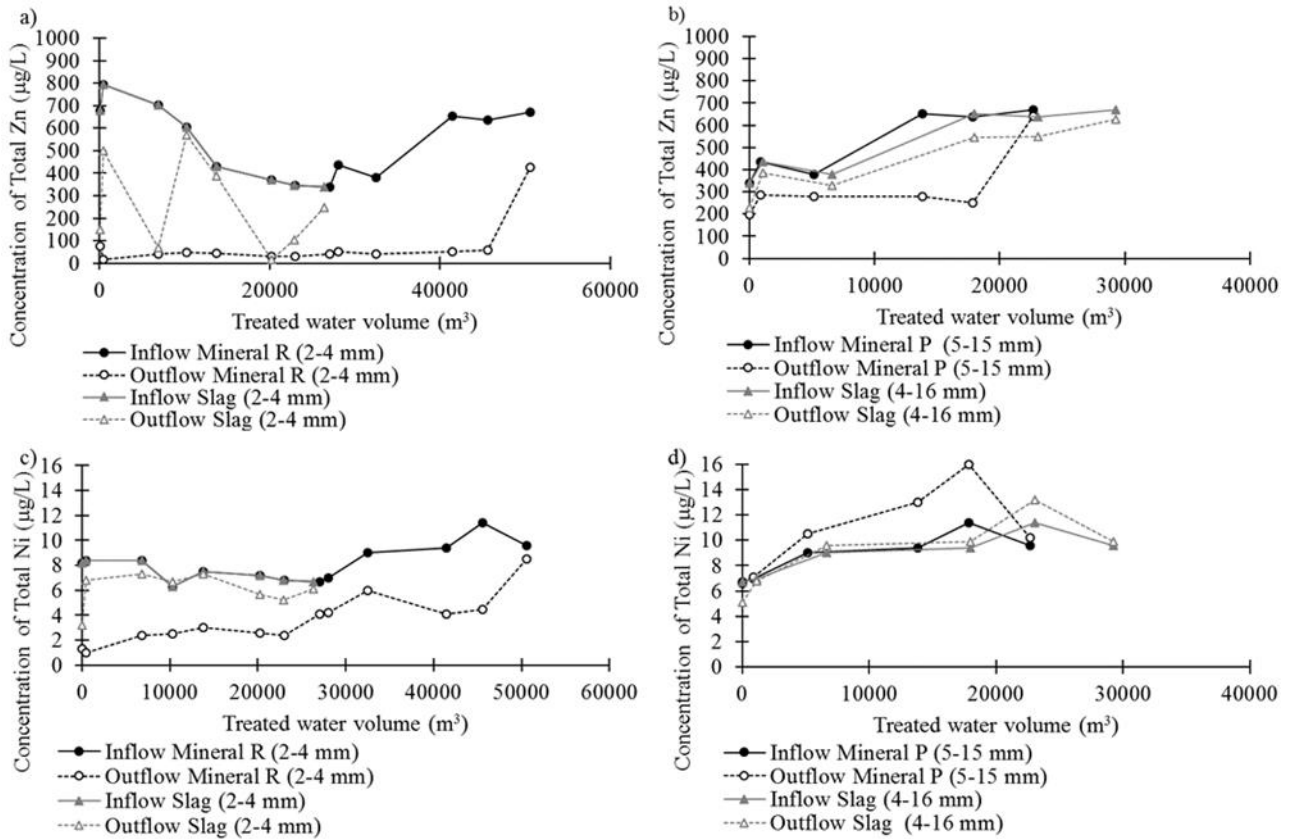
281 ^cLast water sample taken on 11.10.2017. Tracer tests were conducted in laboratory after thawing of
282 the pilot on 1.11.2017.
283

284 The pH of the water discharging from all filter systems increased relative to inflow pH (7.5). Outflow
285 water pH peaked inside the first hour of operation for all materials and the maximum pH value
286 observed for Mineral R (2-4 mm), Slag (2-4 mm), Mineral P (5-15 mm) and Slag (4-16 mm) products
287 was 9.9, 12.1, 8.6 and 9.4, respectively. The increase in pH was due to dissolution of alkaline
288 compounds from the filter materials. After the initial increase, outflow water pH decreased and values
289 between 7 and 8 were recorded after few days of operation in all units except that with the Slag (2-4
290 mm) material, in which pH was over 8 for nearly the whole test. The EC values measured in outflow
291 waters was very similar to those observed in the inflow water for all filter materials tested (Tables
292 S2-S6, Supplementary material).
293

294 *3.2 Inflow and outflow water quality*

295 Concentrations of water quality parameters analysed in inflow and outflow samples collected from
296 the filters are presented in **Tables S2 and S3-S6, respectively** (Supplementary material). For reference,
297 average concentration of Tot.Zn, Tot.Ni and Tot.Fe in inflow samples was 542, 8.2 and 270 µg/L,
298 respectively, while the concentration of Tot.N was 1.1 mg/L and that of DOC was 3.7 mg/L. The
299 average outflow concentration of Tot.Zn, Tot.Ni and Tot.Fe found in samples collected in the pilots
300 containing Mineral R (2-4 mm), Slag (2-4 mm), Mineral P (5-15 mm) and Slag (4-16 mm) was
301 (respectively): 74, 255, 322 and 444 µg Tot.Zn /L, 3.6, 6.0, 10.6 and 9.1 µg Tot.Ni/L and 129, 244,
302 218 and 316 µg Tot.Fe/L. Outflow Tot.N was at the same level as in inflow water. Variations in
303 Tot.Zn and Tot.Ni concentration in inflow and outflow water samples with increasing treated water
304 volume are presented (Fig. 3). Due to the fact that Zn and Ni were present mainly in dissolved form
305 in the inflow water and because total concentrations were analysed more often, only total

306 concentrations are reported (Fig. 3). Moreover, focus is placed on the concentrations of Zn and Ni in
 307 outflow samples, because they were present in higher concentrations in the inflow water than e.g.,
 308 other heavy metals such as Cd, Cu and Pb (Table S2, Supplementary material). Total and dissolved
 309 concentrations of all parameters analysed in inflow and outflow samples are shown in Tables S2 and
 310 S3-S6 (Supplementary material).



311
 312 Fig. 3. Inflow and outflow concentrations (µg/L) of (a, b) total zinc from fine-grained and coarse-
 313 grained filter material, respectively, and (c, d) total nickel from fine-grained and coarse-grained filter
 314 material, respectively.

315

316 3.3 Removal efficiency

317 Best removal of Zn and Ni was accomplished by the smaller-grained samples of the materials tested,
 318 especially by the Mineral R product (Fig. 3; Tables 3- 4 and S8-S9, Supplementary material). Based
 319 on Kruskal-Wallis test, there were statistically significant differences in the removal efficiencies of

320 Zn and Ni between the pilots. In pairwise comparison, it was possible to identify that Ni removal
 321 efficiencies achieved by Mineral R were statistically significant different from those achieved by the
 322 coarser-grained materials, while the removal of Zn achieved by Mineral R was statistically significant
 323 different from that in all other materials tested. Leaching of Ni occurred from the units with Mineral
 324 P material (Fig. 3). Variations in Ni concentration observed in inflow and outflow samples from the
 325 systems filled with Slag material (4-16 mm) were mainly within the determination accuracy ($\pm 10\%$)
 326 of the method used.

327

328 Table 3. Inflow concentration of total zinc (Zn, $\mu\text{g/L}$), load (mg), removed load (mg), load-based
 329 removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. \pm sd (min-max) ($\mu\text{g/L}$)	Load (mg)	Removed load (mg)	RE \pm sd (min- max) (%)	n
Mineral R (2-4 mm)	542 \pm 160 (339-794)	26869	23742	88 \pm 8 (63- 96)	13
Slag (2-4 mm)	533 \pm 182 (339-794)	13883	7101	51 \pm 23 (8- 84)	8
Mineral P (5-15 mm)	519 \pm 151 (339-671)	12300	5249	43 \pm 11 (31-59)	6
Slag (4-16 mm)	519 \pm 151 (339-671)	15849	2171	14 \pm 8 (10- 32)	6

330

331 Table 4. Inflow concentration of total nickel (Ni, $\mu\text{g/L}$), load (mg), removed load (mg), load-based
 332 removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. \pm sd (min-max) ($\mu\text{g/L}$)	Load (mg)	Removed load (mg)	RE \pm sd (min- max) (%)	n
Mineral R (2-4 mm)	8.1 \pm 1.4 (6.3-11.4)	421	231	55 \pm 17 (36-86)	13
Slag (2-4 mm)	7.4 \pm 0.8 (6.3-8.4)	196	24	12 \pm 20 (-1-61)	8
Mineral P (5-15 mm)	8.9 \pm 1.8 (6.7-11.4)	212	-54	-26 \pm 16 (-39-1)	6

Slag (4-16 mm)	8.9±1.8 (6.7-11.4)	274	-19	-7±14 (-11-24)	6
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333

334 Other elements analysed (Cd, Cr, Cu and Pb) were found in very low concentrations in the inflow
335 water, with Cr concentrations being mainly under the detection limit (0.2 µg/L) of the method used
336 (Table S2). Although very low concentrations were present in the water, satisfactory removal of Cd,
337 Cu and Pb was observed, especially by the Slag and Mineral R materials with smaller particle size
338 (Tables 5-7 and S10-S12, Supplementary material). Some retention of Fe was achieved in all pilot
339 systems except that with Slag (4-16 mm), where Tot.Fe leached (although, based on analysis method
340 determination accuracy, values were similar for two-thirds of the measurements) (Table S13,
341 Supplementary material). Clear leaching of Cr was observed from all filter media tested apart from
342 Mineral R. Leaching of As was observed from the Mineral P filter system (Table S14, Supplementary
343 material) while Al leaching occurred from the Mineral R (2-4 mm) material and leaching of dissolved
344 Al also from the Slag (4-16 mm) material (Table S15, Supplementary material). Overall, leaching
345 decreased with increasing treated water volume. Based on Kruskal-Wallis test, there were
346 statistically significant differences between the removal of Al, As, Cd, Cu, Fe and Pb achieved in the
347 filter boxes. In pairwise comparison, it was identified that statistically significant differences in Al
348 removal occurred mainly between Mineral R and Mineral P materials, while for As removal
349 statistically significant differences were mainly between Mineral R and Slag (2-4 mm) and between
350 Mineral R and Mineral P materials. Differences in Cd and Cu removal were identified between
351 Mineral R and the coarser-grained materials, while differences in Fe and Pb removal occurred
352 between Mineral R and Slag (4-16 mm) materials.

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358

359 Table 5. Inflow concentration of **total** cadmium (**Cd**, $\mu\text{g/L}$), load (mg), removed load (mg), load-
 360 based removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. \pm sd (min-max) ($\mu\text{g/L}$)	Load (mg)	Removed load (mg)	RE \pm sd (min- max) (%)	n
Mineral R (2-4 mm)	0.44 \pm 0.11 (0.30- 0.64)	22.5	13.1	58 \pm 17 (27-83)	13
Slag (2-4 mm)	0.38 \pm 0.05 (0.3-0.44)	9.9	2.4	24 \pm 29 (-13-78)	8
Mineral P (5-15 mm)	0.50 \pm 0.12 (0.35-0.64)	11.9	2.7	22 \pm 9 (6-29)	6
Slag (4-16 mm)	0.50 \pm 0.12 (0.35-0.64)	15.4	0.2	1 \pm 8 (-6-14)	6

361

362 Table 6. Inflow concentration of **total** copper (**Cu**, $\mu\text{g/L}$), load (mg), removed load (mg), load-based
 363 removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. \pm sd (min-max) ($\mu\text{g/L}$)	Load (mg)	Removed load (mg)	RE \pm sd (min- max) (%)	n
Mineral R (2-4 mm)	1.8 \pm 0.8 (1.1-3.8)	97	60	62 \pm 10 (49-82)	13
Slag (2-4 mm)	1.4 \pm 0.2 (1.1-1.6)	36	6	16 \pm 9 (4- 32)	8
Mineral P (5-15 mm)	2.4 \pm 1.0 (1.1-3.8)	58	3	5 \pm 13 (-27-8)	6
Slag (4-16 mm)	2.4 \pm 1.0 (1.1-3.8)	74	-3	-4 \pm 6 (-12-4)	6

364

365 Table 7. Inflow concentration of **total** lead (**Pb**, $\mu\text{g/L}$), load (mg), removed load (mg), load-based
 366 removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. \pm sd (min-max) ($\mu\text{g/L}$)	Load (mg)	Removed load (mg)	RE \pm sd (min- max) (%)	n
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Mineral R (2-4 mm)	0.29±0.55 (<0.05-2.1)	7.3	4.0	54±41 (-53-72)	13
Slag (2-4 mm)	0.38±0.70 (<0.05-2.1)	3.9	0.7	18±12 (7-37)	8
Mineral P (5-15 mm)	0.14±0.08 (0.06-0.28)	3.3	1.2	36±62 (-113-52)	6
Slag (4-16 mm)	0.14±0.08 (0.06-0.28)	4.3	0.7	17±59 (-130-23)	6

367

368 3.4 Material characterisation

369 X-ray diffraction (XRD) analysis (Fig. S1) showed that Mineral R is an amorphous material
370 containing aluminium oxide and that Mineral P mainly contains magnesite and quartz, but also some
371 other phases (biotite, chlorite, talc, calcite, periclase and portlandite). Calcium was the main element
372 in the slag materials and XRD showed that many phases were present (akermanite-gehlenite, larnite,
373 bredigite, merwinite, monticellite, cuspidine, magnesiochromite and periclase). All spent filter
374 materials (collected after the pilot tests) showed higher Zn content (Table 8) than fresh samples. In
375 particular, Zn concentrations were higher in the recovered Mineral R product (~800 ppm) than in
376 fresh samples, which was a result of excellent retention of Zn by Mineral R during the pilot tests.
377 Higher Ni concentrations were observed in all spent filter media samples than in fresh samples except
378 for Mineral R. High concentrations of Cr were found in all filter materials (used and fresh) except in
379 the Mineral R product. Full elemental composition can be found in Table S7 (Supplementary
380 material).

381 Table 8. Elemental composition of fresh and spent materials for selected contaminants.

Analyte	Mineral R 2-4 mm	Mineral R 2-4 mm used	Slag 2-4 mm	Slag 2-4 mm used	Mineral P 5-15 mm	Mineral P 5-15 mm used	Slag 4-16 mm	Slag 4-16 mm used
FUSION ICP-OES								
SiO ₂ , %	0.27	1.56	26.94	24.75	27.77	26.32	30.1	26.56
Al ₂ O ₃ , %	87.2	83.92	4.46	4.38	3.5	2.65	4.06	4.59
Fe ₂ O ₃ , %	0.34	0.2	6.64	10.43	7.02	7.57	2.48	3.48
MnO, %	0.003	0.016	1.144	1.213	0.102	0.112	1.007	1.074
MgO, %	0.04	0.29	9.57	10.93	27.54	32.46	11.13	9.21

CaO, %	0.05	0.95	47.68	40.04	11.57	7.28	47.38	46.41
Na ₂ O, %	1.12	0.25	0.06	0.06	0.16	0.08	0.06	0.04
K ₂ O, %	0.01	0.04	0.02	0.02	0.57	0.34	0.01	0.01
TiO ₂ , %	0.006	0.005	1.038	0.954	0.136	0.103	1.03	0.904
FUSION								
ICP-MS								
Cr, ppm	< 20	60	> 10000	> 10000	1440	1660	> 10000	> 10000
Ni, ppm	20	20	3880	6390	800	1320	1740	1920
Cu, ppm	< 10	< 10	210	310	40	30	60	130
Zn, ppm	< 30	800	< 30	60	100	170	< 30	50
As, ppm	< 5	< 5	< 5	7	53	77	< 5	< 5
Pb, ppm	< 5	< 5	< 5	< 5	6	< 5	< 5	< 5

382

383 4. Discussion

384 4.1. Removal efficiency

385 As expected, metal removal was higher in filter systems containing materials with smaller particle
386 size, although in the case of Pb, Mineral P (5-15 mm, consisting mainly of magnesite and quartz)
387 achieved slightly higher removal than the Slag material (2-4 mm, calcium as main element). Because
388 of the larger surface area of smaller particles, and therefore the higher availability of sorption sites, it
389 was expected that smaller-grained materials would be more effective in retaining metals (Chuah et
390 al., 2005). Therefore, pilot operations were started with filter units filled with materials of smaller
391 particle size. Among the small-grained materials tested, Mineral R (aluminium oxide as main
392 component) achieved the best removal rates for the majority of the metals analysed (Zn, Ni, Cd, Cu,
393 Pb). Overall, the removal efficiencies achieved in this study were slightly lower than those reported
394 by Assmuth (2017) for sand and sand-biochar filter media tested for storm water treatment (e.g. 97-
395 99% Zn removal from inflow containing 10-560 µg Zn/L; mostly over 90% Ni removal from inflow
396 containing a mean of ≤5 µg Ni/L). In a previous study, Mineral P was tested in columns for urban
397 runoff and the following removal rates were obtained: Zn 48% (inflow 210 µg/L), Ni 13% (inflow
398 39 µg/L), Cd 20% (inflow 0.056 µg/L), Cu 40% (inflow 69 µg/L) and Pb 67% (inflow 0.48 µg/L)
399 (Gogoi et al., 2018). These removal rates are similar to, or on occasion better than, those reported
400 here.

401

402 The amount of metals retained in the filter media was calculated based on the elemental composition
403 of fresh and spent material (only rough estimation since only one sample/per material was collected).
404 Increased Zn concentrations in spent materials account for 60, 15, 28 and 37% of removed Zn by
405 Mineral R, Slag (2-4 mm), Mineral P and Slag 4-16 mm material, respectively. The increased
406 concentration of Ni and Cu in spent materials of some of the sorbents accounted for hundreds of times
407 the load of Ni and Cu removed from inflow water (Tables 4 and 6). It is important to note that, only
408 one sample of fresh and spent materials were send for characterization analysis and that sampling of
409 spent material was conducted near the inlet area of pilots. As concentration of metals in the water
410 decrease with residence time in the system, it is safe to assume that, larger portion of metals are
411 retained in the inlet area of the filters. Therefore, extrapolating metal concentration values found in
412 the spent material sample collected at the inlet to the whole filter media can result in substantial
413 overestimation of metals retained in the system. By dividing the metal load removed during the whole
414 test period by the mass of sorbent in the system; it is possible to conduct a more viable comparison
415 among metal retention capacity of the tested materials. The amount of Ni, Zn and Cu removed by
416 Mineral R were 12.4, 1276 and 3.2 $\mu\text{g/g}$ of sorbent respectively while 0.8, 239 and 0.2 μg of Ni, Zn
417 and Cu were respectively retained per g the Slag (2-4 mm) material.

418

419 Leaching of As, Ni, Al and Cr was observed from different materials during this study. Leaching of
420 As occurred from the Mineral P filter, but As concentrations in outflow (average 1.5 $\mu\text{g/L}$, maximum
421 5.9 $\mu\text{g/L}$) were under the Finnish drinking water quality limit (10 $\mu\text{g/L}$; D 1352/2015). The Ni
422 concentrations found in outflow samples of systems using materials with larger particle size
423 (maximum concentration 16 $\mu\text{g/L}$) were also under the Finnish drinking water quality limit (20 $\mu\text{g/L}$).
424 Leaching of Al from the Mineral R filter resulted in outflow concentrations below the drinking water
425 limit (recommendation <200 $\mu\text{g/L}$) except in the first sample collected (261 $\mu\text{g/L}$). Similarly, leaching

426 of Cr from the Slag and Mineral P materials did not result in outflow concentration values above the
427 Finnish drinking water quality limit (50 µg/L) apart from the first sample collected from the Slag
428 filter system. Comparison to Finnish drinking water legislation was conducted to highlight the low
429 concentrations of metals leaching from the materials however, it is important to note that leaching
430 results in extra load to the environment and should be taken under considerations during material
431 selection phase.

432

433 The type of filter pilot system tested here can potentially be used for metal removal from other loading
434 sources such as urban storm water, the polishing phase of treatment for wastewater flows from active
435 mine sites etc. In Finland, general metal concentration limits are not set for water discharge from
436 closed mine sites and there are no regulatory limits on metal concentrations in storm water (Inha et
437 al., 2013).

438

439 *4.2 Metal removal mechanism*

440 Possible mechanisms for metal removal were mainly sorption on the surface of the sorbents or, in
441 case of Zn, precipitation as hydroxides due to dissolution of hydroxide from the materials. The
442 characterisation results confirmed that Zn content was higher in the spent materials (especially
443 Mineral R), but the exact mechanism was not revealed. As Zn concentration in the runoff water was
444 significantly higher than that of other metals and the pH of outflow water increased above levels
445 where Zn starts to precipitate (as zinc hydroxide, Zn(OH)₂), precipitation cannot be excluded. On the
446 other hand, the Zn concentration in the outflow water was lower than that required for minimum
447 solubility of zinc hydroxide (Reichle et al., 1975).

448

449 Slag with smaller particle size (2-4 mm) produced fine precipitate, which was collected for analysis.
450 It contained mostly calcium carbonate (CaCO₃) and some magnesium hydroxide (according to XRD),

451 but also a high content of Zn (870 ppm, according to elemental composition). This fine precipitate
452 might have been one reason for the clogging observed with the filter system with 2-4 mm Slag
453 material. With Mineral R material, fine precipitate was not observed, thus clogging must have
454 originated from different mechanisms, which were not revealed in this study. Different ions may
455 attach via different mechanisms (adsorption, precipitation) on calcium carbonate (Sturchio et al.,
456 1997; García-Sánchez and Álvarez-Ayuso, 2002). Zinc might have co-precipitated on the CaCO₃
457 precipitate formed. García-Sánchez and Álvarez-Ayuso (2002) suggest that Zn retention on CaCO₃
458 occurs by precipitation as hydrozincite (Zn₅(OH)₆(CO₃)₂) on the surface, a suggestion generally
459 supported by X-ray photoelectron spectroscopy data.

460

461 *4.3. Functioning of the filter systems*

462 An important parameter in filter-type water treatment systems is the material replacement time, as
463 material replacement inevitably becomes necessary due to decreasing removal efficiency or clogging.
464 The useful working time for different filter systems and filter materials varies between 5 and 10 years
465 (Wendling et al., 2017) or between 1.5 and 9 years (Monrabal-Martinez et al., 2017). However, these
466 values are based on the sorption capacity of materials tested under laboratory or pilot test conditions
467 (possible clogging of real or full-scale systems is not taken into consideration). From the results
468 obtained in the present study, it was not possible to evaluate accurately the material replacement time
469 of full-scale systems. However, it was possible to make rough estimates for the small-grained
470 materials, which reached the clogging stage during the experiment. In the example of a filter system
471 within a ditch network treating 10 m³ of inflow water (of similar quality to the inflow water used in
472 this study) per day, the system would require the following dimensions: 6 m x 1.5 m x 0.8 m (length
473 x width x height). The filter material replacement time would be 5.5 years for Mineral R (2-4 mm),
474 while it would be 2.8 years for the Slag (2-4 mm) product. The material replacement times were
475 estimated based on the relationship between treated water volume and the material volume identified

476 during the pilot tests (Table 2). Another important factor to be considered on up-scaling the filter
477 systems is the decrease in hydraulic capacity over time (Hatt et al., 2008) and, at high latitudes,
478 clogging of the filter due to freezing.

479

480 **5. Conclusions**

481 Continuous in situ pilot-scale tests of filter systems were conducted in the field, where varying inflow
482 water quality and temperature offered more realistic conditions for evaluating the suitability of filter
483 materials than column or batch experiments in the laboratory. Filter performance was dependent on
484 material composition and particle size (smaller particle size being more effective). The highest metal
485 removal efficiencies and largest amount of water treated (per volume of material applied) were
486 achieved by aluminium oxide-based recycled mineral material (2-4 mm). In general, while smaller-
487 grained materials performed better in terms of removal efficiency, the removal rates achieved by
488 coarser-grained commercially available mineral material (5-15 mm) were comparable to those
489 achieved by slag material with small particle size (2-4 mm).

490

491 Due to the diluted nature of the water treated and the composition of the materials tested, leaching of
492 some metals occurred. For example, Al concentrations were higher in outflow than inflow for units
493 filled with recycled mineral material. Similarly, As was leached from commercial mineral product
494 and higher Cr concentrations were found in the outflow of all filter systems except those with recycled
495 mineral material. Leaching can also be expected from full-scale systems if the materials are used for
496 treatment of similarly dilute streams to that tested in this study

497

498 Based on the results obtained, full-scale systems using the recycled mineral product (2-4 mm) would
499 have an approximately two-fold longer material replacement time (effective working time; treated
500 water volume/volume of material ≈ 2800) than systems using the slag (2-4 mm) product (treated water

501 volume/volume of material ≈ 1400). Material replacement time could not be estimated for the coarser-
502 grained materials due to test interruption (freezing). Therefore, clogging because of precipitate
503 accumulation or armouring was not reached. Overall, the recycled mineral material tested can be
504 recommended for full-scale tests, especially for applications where high Zn removal is required.

505

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518

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