

Supplementary Information: Material characterization

Improving the sustainability of granular iron/pumice systems for water treatment

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22 **SI Material characterization**

23 **SI1 Experimental Section**

24 The microstructure of used Fe⁰ and pumice was characterized using mercury intrusion porosimetry
25 (MIP) measurements and by scanning electron microscopy (SEM) observations.

26 Moreover grain size distribution and the geotechnical parameters (i.e. coefficient of uniformity and
27 mean grain size) derived from it have been determined.

28 **SI1.1 MIP**

29 MIP is performed by injecting mercury into a desaturated porous material. The in-pore invasion
30 process is supposed to be governed by the Washburn-Laplace equation in which the size of intruded
31 pore accessed, assimilated to cylindrical pores are inversely proportional to the applied pressure
32 according to Eq. 5 (Washburn, 1921):

33
$$P = -\frac{2\gamma \cos \theta}{R_p} \quad (\text{SI1})$$

34 where P is the mercury injection pressure (Pa), γ is the surface tension of mercury (0.485 N/m), θ is
35 the contact angle between solid and mercury ($\theta = 130^\circ$) and R_p is the pore access radius for
36 cylindrical pores (m). MIP measurements have been carried out using a Micromeritics instrument
37 apparatus type (AutoPore IV 9500). The instrument is capable of a minimum intruding pressure of
38 3.4 kPa and a maximum pressure of 227 MPa, so that the pore radius ranges from 2.7 nm to 180
39 μm .

40 For pumice particles the measured pore data allow determining the inter-particle and intra-
41 particle porosities of the pumice particles, the apparent specific weight ρ_{as} (defined as the ratio of
42 the mass and the apparent volume of the pumice particles) and the specific weight ρ_s (defined as the
43 ratio of the mass and the volume of the solid phase of the pumice particles).

44 **SI1.2 SEM**

45 During SEM (Hitachi, type: s3400N) observations, secondary electron mode was used. Pumice
46 particles were coated with carbon. The observations enable a characterization of the morphology of
47 both materials and of the inner pore structure of pumice.

48 **SI2 Results and Discussion**

49 **SI2.1 SEM Observations of Fe⁰ and pumice particles**

50 SEM images detailing the microstructures of, respectively, Fe⁰ and pumice particles are shown in
51 Fig. SI1. These observations show that the Fe⁰ and pumice particles are irregular. It can be observed
52 that the pumice particles (grains) are porous with oval shaped and fibrous cavities (or pores). The
53 diameter of these cavities at the surface is lower than about 40 μm (radius 20 μm).

54

55 **SI2.2 MIP measurements of pumice particles**

56 As shown in Fig. SI2, where for graphical convenience the pore size distribution is as usual
57 expressed as $\frac{dV_i}{d(\log r)}$ where V_i is the volume intruded by mercury and R is the pore
58 equivalent radius, pumice exhibits a well defined peak around 70 μm and pores with equivalent
59 radius inferior to 20 μm. According to the SEM observations, these results show that the pores with
60 radius inferior to 20 μm can be attributed to the inner porosity of the pumice particles, so that the
61 pores with equivalent radius superior to 20 μm can be attributed to the inter-particle porosity. The
62 total porosity of the pumice medium Φ_0 (%) in the conditions used in MIP tests, is defined as:

63
$$\Phi_0 = V_{\text{mercury intruded}} * M / V \quad (\text{SI3})$$

64 Where $V_{\text{mercury intruded}}$ is the total intrusion volume (mL/g), M the mass of pumice (g) and V the
65 volume of the pumice medium (mL).

66 The volume of the inter-particle volume Φ_{inter} (%) is given by:

67
$$\Phi_{\text{inter}} = V_{R>20\mu\text{m}} / V \quad (\text{SI4})$$

68 Where $V_{R>20\mu\text{m}}$ (mL) is the volume of intruded mercury in pores with radius superior to 20 μm .

69 It can be noticed that the compactness C_{pumice} (-) of the pumice particles, defined as the ratio of the
70 apparent volume of the particles to the total packing volume (V = volume of the medium), is given
71 by:

$$72 \quad C_{\text{pumice}} = 1 - \Phi_{\text{inter}}. \quad (\text{SI5})$$

73 Furthermore, the volume of the intra-particle ϕ_{pp} is given by:

$$74 \quad \phi_{\text{pp}} = V_{R<40\mu\text{m}} / V / C_{\text{pumice}} \quad (\text{SI6})$$

75 Where $V_{R<20\mu\text{m}}$ (mL) is the volume of intruded mercury in pores with radius inferior to 20 μm .

76 The results are given in Tab. SI2. The total porosity of the pumice medium has been estimated to be
77 73.3 % and the inner porosity of the pumice to be 41.0 %.

78

79 **SI2.3 Grain size distributions of Fe^0 and pumice particles**

80 The grain size distributions of Fe^0 and pumice particles are shown in Fig. SI3.

81 The main geotechnical parameters derived by the grain size distributions are the coefficient of
82 uniformity $U = d_{60}/d_{10}$ (i.e. ratio between the diameters corresponding to 60 and 10 % finer in the
83 grain size distribution) and the mean grain size d_{50} (i.e. the diameters corresponding to 50 % finer in
84 the grain size distribution).

85 The mean grain size (d_{50}) is about 0.5 mm and 0.3 mm for ZVI and Pumice respectively, their
86 coefficients of uniformity (U) are, respectively 2 and 1.4 and therefore both materials are
87 characterised by a uniform grain size distribution.

88

89 **SI2.4 Porosity of the columns**

90 Under the hypothesis that the relative density (packing) of granular mixtures are the same in the
91 columns and in the MIP tests, the estimated porosity of the reactive zone can be given for systems
92 A through E (Tab. 1, main text) according to:

93
$$\Phi_0 = \Phi_{inter} + \phi_{pp} \cdot f_{pp} \quad (SI7)$$

94 where f_{pp} (-) is the pumice particle volume fraction determined by $f_{pp} = V_{pp}/V$ with V_{pp} the volume
95 of the pumice particles and the V the volume of the reactive zone.

96

97 **References**

98 Washburn E.W., 1921. The dynamics of capillary flow, Phys. Rev. 17, 273–283.

99

100

100 **Table SI1:** Composition and experimental duration of the studied columns. *-marked systems were
101 stopped because of excessive permeability loss.

102

System	Composition (Fe ⁰ :pumice)	Duration (day)
A	0:100	45
B	10:90	90
C	25:75	36*
D	50:50	28*
E	75:25	22*
F	100:0	17*

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104 **Table SI2:** Characteristics of Fe⁰ and pumice particles tested by MIP.

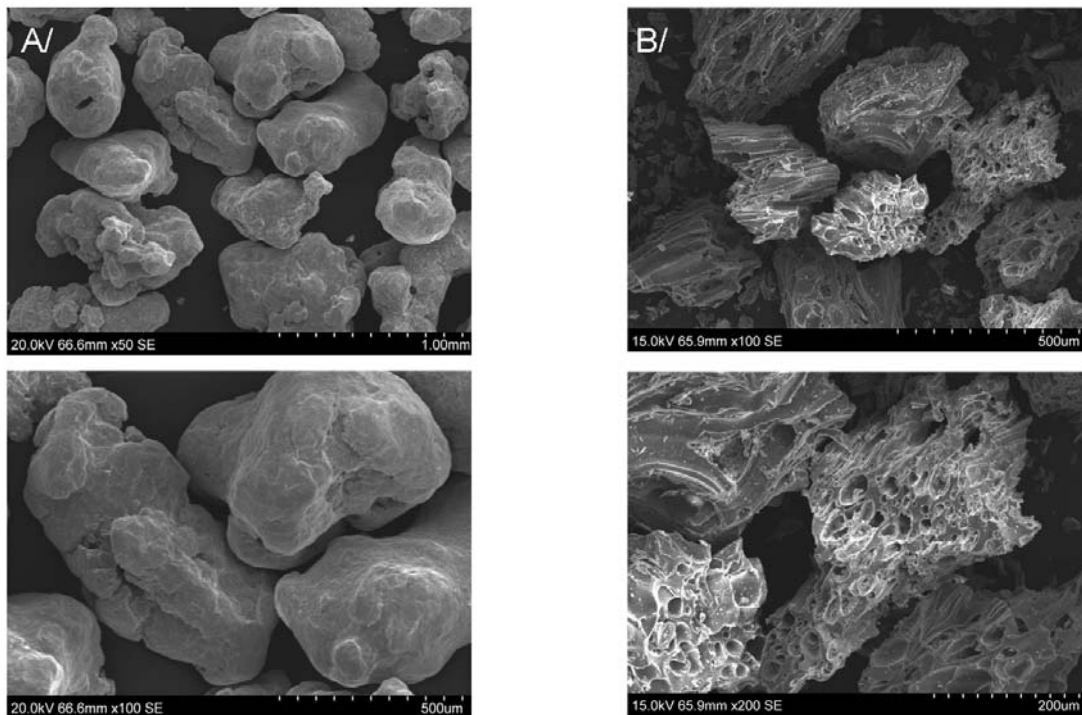
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	Fe ⁰	Pumice
Specific weight ρ_s (g/cm ³)	7.78	1.92
Apparent specific weight ρ_{as} (g/cm ³)	7.78	1.14
Compactness C (-)	0.51	0.45
Inter particular porosity Φ_{inter} (%)	49.6	54.8
Intra particular porosity ϕ_{pp} (%)	-	41.0
Porosity Φ_0 (%)	49.6	73.3

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107 **Figure SI1:** SEM images of the Fe⁰ particles (A) and of the pumice particles (B).



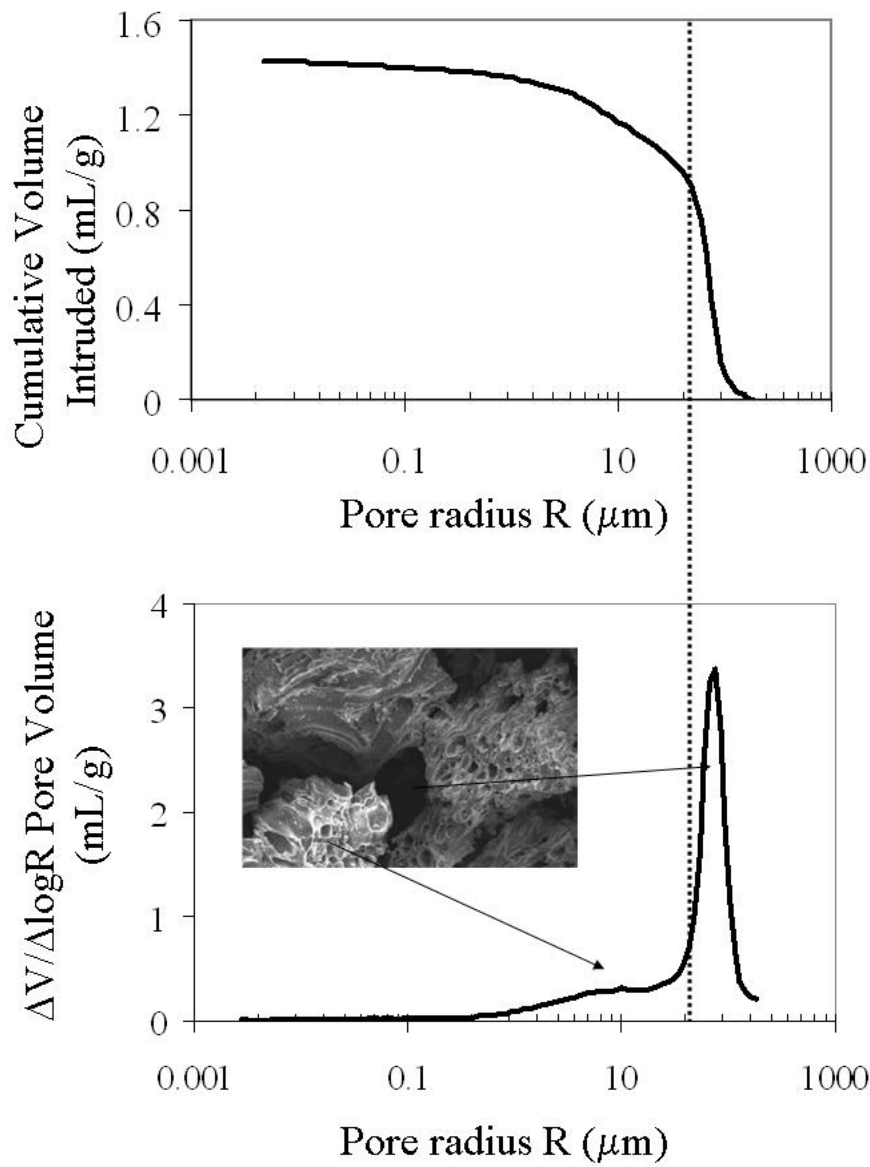
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110 **Figure SI2:** Cumulative volume intruded (mL/g) and pore size distribution of the pumice particles.
111 Two types of porosity are observed: inter particular porosity Φ_{inter} ($R > 20\mu\text{m}$) and intra particular
112 porosity ϕ_{pp} ($R < 20\mu\text{m}$).

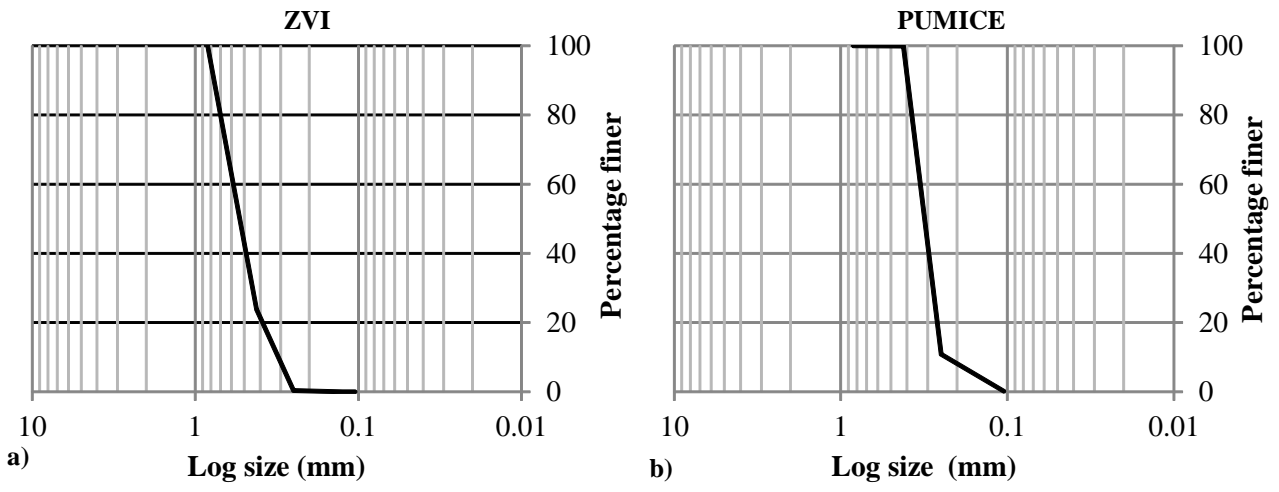
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118 **Figure SI3:** Grain size distributions of used materials: Fe⁰ (a) and pumice (b).

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