Mathematic Analysis of Porosity Loss in Granular Metallic Iron (Fe^0) Water Filter

Richard Domga[a], Fulbert Togue-Kamga[b], Jean-BoscoTchatchueng[a]

[a] *Laboratory of Industrial and Pollution Chemistry, Department of Applied Chemistry, ENSAI, University of Ngaoundéré, BP 455 Ngaoundéré, Cameroon.*

[b] *Institute of Fisheries and Aquatic Sciences at Yabassi, University of Douala, Box 2701 Douala, Cameroun.*

Corresponding Author: *Richard Domga, Laboratory of Industrial and Pollution Chemistry, Department of Applied Chemistry, ENSAI, University of Ngaoundéré, BP 455 Ngaoundéré, Cameroon. E-mail: domga.richard@yahoo.fr*

ABSTRACT

Zero-valent iron (Fe^0) has been used as a new efficient and affordable filter material for water treatment in last two decades. Design guidance for cost-effective Fe^0 filters still remain a challenge in the scientific community. Nevertheless, there is a need to give the scientific foundation for the design and assessment of Fe^0 water filters technology. In this work, we suppose equal corrosion of single Fe^0 particles and exploit the radius loss ΔR to evaluate the degree of porosity reduction in the entire system. It is shown, long-lasting filters should satisfy less than 53% Fe^0 (v/v) for R_0=1 mm.Some parameters such as the coefficient of volumetric expansion with is function of the oxygen accessibility, the initial radius, the primary volume of Fe^0, the initial porosity of the system are use to establish a mathematical equation of Fe^0 filters.The hydraulic conductivity of the Fe^0 filters system should be improved by included this equation in modeling.The discussion of available data on porosity reduction of Fe^0 system should be enhanced with this model.

Keywords: *Hydraulic conductivity; Mathematical equation; Porosity reduction; Water treatment; Zero-valent iron.*

INTRODUCTION

Filtration concerns the separation of suspended solids by straining through a granular filter due to the screening effect of the porous media. Granular sand filter are classified in two types depending of the particle dimension: coarse sand filter and fine sand filter. The particle size of materials involves straining effectiveness. Smaller suspended particles are more filter out by small intergranular spaces in fines and filters rather than in a coarse sand filter which have large pores spaces. In some case, filtration is improved for safe drinking water when some chosen material such as active carbons, metal oxides, peat or material combination such as pumice/peat or sand/oxide which provide ionic exchange for some dissolved species are used [1,2]. The mechanism of pollutants removal in filtration system is still complex. The varying states of natural water and processes taking place inside the filter make it very complicated to design and optimize [3,5]. Academicals information concerning the processes of contaminant elimination is still limited [4, 5].

In the case of new filtration system such as those containing metallic iron, the theoretical knowledge is worse. Iron precipitates are one of the fouling agents which are in situ formed and transformed in those filters. Modeling suitably water treatment processes involve the knowledge of the law of iron precipitates or iron corrosion [6]. Zero valent Iron was the principal material to be used in permeable reactive barrier (PRBs) for in situ groundwater remediation. It remains the main material used in the construction of these barriers 20 years ago [7, 8]. More than 200 PRBs containing Fe^0 are used in the worldwide for groundwater remediation and have being testify suitable for contaminants removal although theoretical knowledge to design and optimize Fe^0 filters is still partial [16] [9,10]. O´ Hannesin and Gillham [8] showed experimentally a quantitative "reductive chlorination" through a PRB containing only 22% Fe^0 (w/w). This result demonstrated that admixing aggregates to Fe^0 was beneficial for the efficiency of Fe^0 filters. In the other hand, Ulsamer [12] ascertained that the effect of

admixing aggregates on the effectiveness of Fe^0 filters is still unknown. Beside, the tested mixtures of four dual Fe^0/aggregate fixed beds for ''reductive dechlorination'' (Fe^0/gravel, Fe^0/anthracite, Fe^0/pumice, Fe^0/sand) have been evaluated by Ruhl et al. [13]. He concluded that none of the four dual were appropriate for field scale application. In fact, there is no room for endless debate about the suitability of hybrid Fe^0 systems in available literature on Fe^0 filters if the volumetric expansive nature of iron corrosion is correctly took into account [1, 14, 15]. Solute transport process engages in filtration on Fe^0 systems remains difficult to explain and it influences water treatment operation.

Many hypotheses are developed in the previous works to describe the equilibrium thermodynamics and modeling these processes. Mass transfer kinetics should be accurately handle at the time thermodynamics are quantitatively explained. Filtration performance could be strongly optimized only when a correct model of equilibrium thermodynamics is provided.

The sustainability of 100% Fe^0 filters has been challenge less than ten year ago by academic investigation. However no doubt has been report on it efficiency. Theoretical analysis revealed that to improve sustainability of filters, other aggregates (e.g. anthracite, gravel, pumice, sand) should be admixing to Fe^0.Rahman et al. [1] discovered from theoretical considerations that the most sustainable volumetric for admixing Fe^0/aggregate is 25/75. These theoretical calculations were lately experimentally confirmed [18,19]. Investigation has been focus on the total Fe^0 mass instead of the radius of single particles useful in grain size analysis. Methods for modeling mechanism taking place into Fe^0 filter from the radius of a single particle to the entire system could be regarded as the appropriate reasoning. The main variable involved in the performance of Fe^0 system is certainly the radius depletion yielding to iron corrosion. Beside, the initial concentration of contaminant, the iron corrosion rate, the water velocity of contaminant should be also considered while modeling the process of mass transfer within the system. Though, no attention is paid to the kinetics aspects in this study.Domga et al 2015 [26] established a universal equation showing the extent of radius loss of a (spherical) Fe material or the attacked penetration depth ($X = R_0 - R$) depends on the following interrelated factors: (i) initial size of the particles (R_0), (ii) extent of Fe^0 depletion (V_{oxide}), initial amount of

Fe^0 (V_{ZVI}), and (iii) the availability of dissolved oxygen (η value). This equation should be routinely incorporated in simulations for modeling the hydraulic conductivity of Fe.The work of Togue et al [37] established model and simulation of iron/sand filter.

Iron depletion is regarded as the basic process involves in the performance of Fe^0 filters due to the fact that volumetric expansive nature of iron precipitates gradually filled the primary inter-granular spaces of Fe^0 filter initially similar to an extremely permeable sand bed. As the porosity and the pore throat dimension decrease, the amount of dead end pores increase [20]. The interstices are sealed by iron corrosion products and the primary fully permeable system is gradually altered to a less interconnected porous system. The initial porous system is transformed to an extremely porous even though less permeable [21] since connectivity is gradually damaged by iron corrosion products.

This work recapitulates and amends earlier research on Fe^0 filters to give to the scientific community and engineers the basis to enhance the performance of Fe^0 filters. It demonstrates how discussion on the suitability of hybrid Fe^0 systems becomes fundamental only if the initial system is appropriately characterizing from lab and field experiments. For this aim, the variation of the residual porosity of a Fe^0 filter is described as inter-granular spaces are filling by iron corrosion products stem from cylindrical particles corroded.

EVALUATING THE HYDRAULIC PERFORMANCE OF ZERO-VALENT IRON HYBRID SYSTEMS

Handle hydraulic conductivity of zero-valent iron hybrid systems could help to properly design granular Fe^0 filters for water treatment. Available studies evokes that the hydraulic conductivity of a Fe^0 filter is a coefficient dependent on the porous system properties where the flow takes place (particle size, particle shape, distribution and shape of the pores), the properties of inflowing water (viscosity, density) and the saturation of the porous medium. In fact, these influencing variables are inter-dependant [23-26].Among granular in hybrid systems (e.g. Fe^0/anthracite, Fe^0/gravel, Fe^0/pumice, Fe^0/sand) [1,6,24,26], the investigation is targeting on the Fe^0 diameter. The dwelling time of water in the Fe^0 system determines the degree of matrix and liquid exchanges. The matrix involves the in situ

iron precipitates including the aggregates and the biofilms. The inflowing water chemistry influences the volumetric expansion of iron corrosion products including the interactions of contaminant with the matrix.

Published studies in the past two decades [22-26] revealed that physical characteristics of Fe^0 determine both the hydraulic conductivity and the water treatment performance a Fe^0 filter. Significant factors involve the depth of the Fe^0-containing layer, the filter media setting arrangement, the size and the smoothness of the media particles. Discussions in published studies are base on the major characteristics having an effect on hydraulic permeability of Fe^0 filters [6,12,13,25,27]. However, the effect of each tested factors on the performance of Fe^0 filters is demonstrated in available studies.

The challenge could be focused to assess the contribution of the volumetric expansion of iron corrosion products on the process only if some others mains causes of clogging of field Fe^0 filters such as precipitation of foreign species (e.g. $CaCO_3$), growth of biofilms, accumulation of suspended particles and (vi) accumulation of pollutant molecules and the accumulation of H_2 are operationally neglected. This could be done in the laboratory where experimental conditions are arranged to remove some of those mains factors. If the contribution of iron corrosion products is substantial, volumetric expansion

$$\Delta_m = \sum_1^{NZVI} \pi \rho h(-X^2 + 2R_0X) = \frac{\rho}{R_0^2} V_{ZVI}(-X^2 + 2R_0X)$$ (2)

V_{ZVI} and R_0 are the parameters variables of this equation. X=0 associates to the initial particle as R= R_0 and X = R_0 to Fe^0 total depletion as R= 0. The volume of oxide (V_{ox}) produced and the initial pore volume (V_{pore}) of the filter parameters are involve in Fe^0 depletion. If $V_{ox}^\infty <= V_{pore}$, Fe^0 complete depletion can be achieved else Fe^0 depletion should be partial since a fraction of the initial quantity of Fe^0 will not react because space is needed for volumetric expansion. This surplus Fe^0 demonstrates a pure material wastage [1,20]. In the case that ($V_{ox}^\infty = V_{pore}$) associates to entire pore fouling by iron

$$-X^2 + 2XR_0 - (V_{oxyde}/V_{ZVI}) \times (R_0^2 / (\eta - 1)) = 0$$ (5)

Eq. (5) is suitable to discuss system clogging following Fe^0 depletion. This equation shows that the degree of radius reduction of a Fe^0 particle are determined by the following factors: the initial dimension of the particles (R_0), the volume of oxide produce (V_{oxide}), the initial

nature of iron corrosion at pH > 4.0 [15] should be systematically considered in all environmental Fe^0/H_2O systems.

METHODS AND MATERIALS

Calculation of X=R_0-R

The method implemented in this section involves the estimation of the radius loss(X=R_0-R) of a single Fe^0 cylindrical grain and investigate their suggestion in the progression of porosity reduction.

Evaluation of X=R_0-R

Let' consider in this study cylindrical particles with equal radius R_0. The volume of these particles (V_{part}) is given by $V_{part} = \pi h R_o^2$, where h is the height of particles. The number of particle (N_{ZVI}) filling a volume V_{ZVI} is $N_{ZVI}=V_{ZVI}/V_{part}$. The mass of a particle (m_{part}) is expressed by $m_{part} = \rho V_{part}$, where ρ is the specific weight of the material. At the initial time ($t_0=0$), the mass of a particle is $m_{opart} = \pi \rho h R_o^2$ and it volume at time t>0 is $m_{part} = \pi \rho h R^2$. The mass loss correspondent can be determine as

$$\delta_m = m_{opart} - m_{part} = \pi \rho h(R_0^2 - R^2).$$

Substituting R into the previous equation, δ_m reads as:

$$\delta_m = \pi \rho h(-X^2 + 2R_0X)$$ (1)

For a system containing N_{ZVI} particle, the mass loss is read as Eq.(2):

corrosion products, R_0 is equal to X. Hence, the discussion about system clogging should be appropriate with Eq. 2 only if R_0 is larger than X_1 (R_0> X).

For a system containing N_{ZVI} particle, the mass loss is read as Eq.(2):

$$\Delta_m = \rho \times \Delta V_{ZVI} = \rho \times V_{oxyde}/(\eta - 1)$$ (3)

$$\Delta V_{ZVI} = V_{oxyde}/(\eta - 1)$$ (4)

Rearranging Eq. 2, Eq. 3 and Eq. 4 yields the following second degree equation in X (Eq. 5):

volume of Fe^0 (V_{Fe}^0), and the accessibility of dissolved oxygen (η). As the intrinsic reactivity of Fe^0 material is not developed in Eq. (5), this equation should be frequently used to design experiment with Fe^0. Eq. (5) should be also regularly used to assess the results with different

materials under comparable conditions. Ideally, such a systematic research should be performed under unified experimental conditions (standard protocols). To extend the life service of systems, non expansive materials (e.g. sand) should be admixed to Fe^0. In this case, Eq. (5) has to heed the case of mixture systems. The volumetric ratio of Fe^0 in the solid mixture, $V_{ZVI} = \tau_{ZVI}*V_{solid}$ and Eq. (5) is rearranged as:

$$X^2 - 2XR_0 + \left(\frac{V_{oxyde}}{V_{solid}}\right) \times \frac{R_0^2}{[\tau_{ZVI} \times (\eta - 1)]} = 0 \quad (6)$$

Representation of Modeling Outcome

Eq. (5) was solved graphically using an Excel table for some chosen significant cases by discovering the interception of f(X) with the x axis. Non porous materials are considered. Since $0 < X < R_0$ following the section 3.1, Eq. (5) include two solutions but only one solution is physically acceptable. To solve Eq. (5) a theoretical system with a total volume of 1000 mL and a porosity of 36% containing Fe^0 particles with equal radius of 1.0 mm is assumed. The hypothesis system is purely mathematical as no physical system is associated to this thickness [41]. In such a system the initial $V_{Fe}^0 = 640$ mL yielding an initial pore volume $V_{pore} = 360$ mL. The volumetric expansion coefficient η values (2.08, 3.75, 4.20 and 6.40) used are provided by Caré et al. [20]. Graphical solutions were validated by analytically solving the equation using Maple16 software. Maple is a computer algebra software developed since 1980's for engineering and academia.

3.2.1. Expression of the Extent of Fe⁰ Depletion

Eq.(5) is solve graphically to find the values of X. The proportion law is used to determine the Fe^0 mass associated to the residual R value as:

$$m = m_0(S)^2 \quad (7),$$

Where $S = (R/R_0)$

The weight percent of remaining Fe^0 and the percent of Fe^0 corroded are wrote Eq (9) and Eq(10) as :

$$P_R = 100 (m/m_0) = 100 (S)^2 \quad (9)$$

$$P_C = 100 - P_R \quad (10)$$

Similarly, the volumetric percent of remaining Fe^0 is wrote Eq (11) as:

$$V = V_0(S)^2 \quad (11)$$

Eq. 6 is rearranged to deduce the volume of pore engaged by expansive corrosion (V_{oxide}) associated to each value of X. Effectively

$$A = (-X^2 + 2XR_0)/R_0^2.$$

$$V_{oxide} = A* V_{solid}*[\tau_{ZVI}*(\eta - 1)] \quad (12)$$

In fact, for X = 0, $V_{oxide} = 0$. Suitable values of V_{oxide} are given for $V_{oxide} \leq V_{pore}$, V_{pore} being the initial porosity of the filter.

RESULTS AND DISCUSSION

Appropriateness of Fe⁰/Sand Systems

Eq. (6) is solve graphically for five different values of τ_{Fe}^0 under anoxic conditions ($\eta = 2.08$). Results are recapitulated in Figure 1. The line y = 0 is included to improve the discussion. Each curve reaches the line y= 0 for a X/R_0 (in %) value which corresponds to entire porosity loss or system clogging ($V_{oxide} = V_{pore}$). Figure 1 clearly demonstrates that for $\tau_{Fe}^0 = 1$ (100% Fe^0), the system is clogged for $X/R_0 = 30.00\%$ (Table 1).
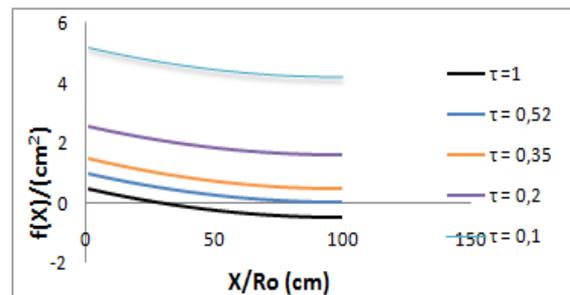
Figure1. *Effect of the volumetric fraction of Fe^0 in the material mixture (τ_{ZVI} values) on the Fe^0 depletion (X/R_0) extension interception of f(X) with the X axis for five values of τ_{Fe}^0 (η= 2.08).*

Table1. *Effect of volumetric proportion of iron (τ_{Fe}^0) in the solid fraction on Fe^0 depletion. The Excel table for Figure 1 is used to read the value of X. P_R and P_C are respectively the residual and the consumed mass percent of Fe^0 after Eq. 9 and Eq. 10.*

τ_{ZVI}	1.00	0.52	0.35	0.20	0.10
X (mm)	0.30	0.99	1.00	1.00	1.00
R (mm)	0.70	0.01	0.00	0.00	0.00
P_R (%)	49.00	0.01	0.00	0.00	0.00
P_C (%)	51.00	99.99	100.00	100.00	100.00

Five values of $\tau_{Fe}{}^0$(η= 2.08) under anoxic environment are used to solve graphically Eq.(6) and therefore determine Fe^0 depletion extension as function of it initial volumetric fraction in the system. Uniform corrosion is assumed and material is supposed to be compact cylindrical particles. The initial systems porosity Φ_0= 36%. In real systems, irregularly shaped particles are fundamentally more porous (Φ_0> 36%) [34–35]. It is evident that for $\tau_{Fe}{}^0$> 0.5100, system clogging occurs before Fe^0 complete depletion (f(X) intercepts y = 0).Working conditions: V_{system} = 1.0 L, initial porosity (Φ_0) = 36%, R_0 = 1.0 mm. It is observed that the system is clogged just at Fe^0 depletion for $\tau_{Fe}{}^0$ = 0.5100, while systems with $\tau_{Fe}{}^0$< 0.5100 do not clog at all (no interception of f(X) with X axis). Fully Fe^0 depletion occurs during the active remediation time in those systems depending on the influence of environmental conditions and the intrinsic reactivity of the used material.

The X/R$_0$ values corresponding to the interception of each curve with the x axis determine the percentage of particles size corroded at the system clogging. The system is bunged for X/R$_0$ = 30.00%, $\tau_{Fe}{}^0$=1 or for 100% Fe^0 as shown in Fig.1. Numerical solution of Eq.1 reveal that it corresponds to 51.00% of iron mass corroded ((Eqs. (9) and (10)) since there is no space for iron corrosion products. Previous investigations corroborate present report as they show that in a pure Fe^0 system, more than 51.00% of the initial Fe^0 mass are wasted [6,16,17]. Although permeability loss is not necessarily due to complete pore filling, but mostly due to reduced interconnectivity of pores, these results critically question the

rationale for constructing Fe^0 PRBs, including Fe^0 filters containing zones with 100% Fe^0. It is crucial to remind here that permeability loss of Fe^0 filters for contaminant free systems has been documented [27].

In this section the formation of foreign precipitates (e.g. CaCO$_3$) and suspended particles within the filter is neglected. Cylindrical particles with 1.0 mm initial radius and an ideal porosity of 36%, are assumed. Higher values of the porosity are reported in the real world [6]. However, pure Fe^0 filters are not sustainable is considered as the universal statement of this section.

Dissolved Oxygen Level and Porosity Loss

Figure 2 and Table 2 summarize the extent for Fe^0 consumption (X/R$_0$) as function of the volumetric extension coefficient of iron corrosion (η values).

Figure2. *Effect of the volumetric expansion coefficient of iron corrosion (η values) on the Fe^{0}consumption (X/R$_0$) extension.*

Table2. *Effect of the coefficient of volumetric development (η) of iron on Fe^0 consumption.*

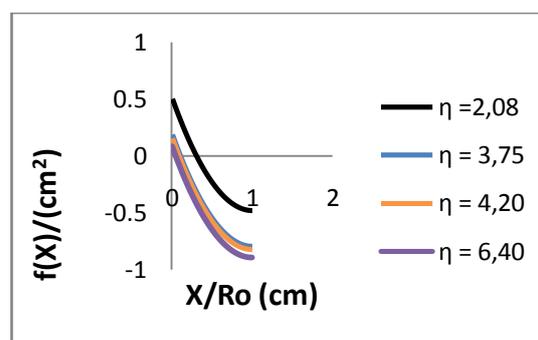| η	2.08	3.75	4.20	6.40
Oxide	Fe$_3$O$_4$	Fe(OH)$_2$	Fe(OH)$_3$	Fe(OH)$_3$6H$_2$O
X(mm)	0.30	0.10	0.09	0.05
R(mm)	0.70	0.90	0.91	0.95
P$_R$(%)	49.00	81.00	82.81	90.25
P$_C$ (%)	51.00	19.00	17.19	9.75

Eq. (6) is solved for four values of the coefficient of volumetric development (η) of iron operationally changing from pure anoxic (η = 2.08 - Fe$_3$O$_4$) to pure oxic conditions (η= 6.40 - Fe(OH)$_3$).6H$_2$O) [20]. X values is copied from the Excel table for Fig. 2. P$_R$ is the residual and P$_C$ the consumed mass percent of Fe^0 after Eq. 9 and Eq. 10.

It is shown in Figure 2 that the system with the largest extent of Fe^0 (f(X) intercepts y = 0) is associated with η> 2.08 (anoxic conditions). Working conditions: V_{system} = 1.0 L, initial porosity (Φ_0) = 36 %, R_0 = 1.0 mm and τ_{ZVI} = 1. Material is assumed to be ideal concentric layers of Fe^0 and uniform corrosion is supposed.

It is clear from Fig. 2 that only systems working under pure anoxic conditions could accomplish

a X estimation of 0.3000 mm (X/R$_0$ = 30.00 - Tab. 2) relating to 51.00 % consumption of the initial quantity of Fe^0. The degree of Fe^0 consumption in all other systems was under 30 %.

In this section, the volumetric proportion of iron τ_{Fe}^0 = 1. The discussion could be rehashed for other τ_{Fe}^0 values. Rahman et al. [1] summarized the discussion in previous works and showed that the trend is the same. Thus, the arrangement of Eq. 5 (or Eq. 6) plainly demonstrates that, for R$_0$ ≤ 1, manageable Fe^0 filters are those containing under 51 % Fe^0 (v/v) and working under pure anoxic conditions. While this information isn't new, information identified to testing Fe^0 filters under pure oxic conditions are abundant in the literature. Eq. 5 can be challenge in an environment where CaCO$_3$ precipitation is expected as raw water would first be able to be liberated from Ca^{2+}, preceding the Fe^0-containing systems. In this case, for more sustainable Fe^0 filters at sites, suitable

systems for Ca^{2+} evacuation utilizing zeolite for instance are plenteous [29-30].

Impact of the Initial Fe^0 Particle Size

Beside τ_{Fe}^0 and η values, an essential parameter for the effectiveness of a Fe^0 filter is the range of the particles used (R$_0$ - Eq. 5). Figure 3 and Table 3 summarize the results of the graphical solution of f(X) as a function of X/R$_0$ (in%) for five different values of R$_0$.
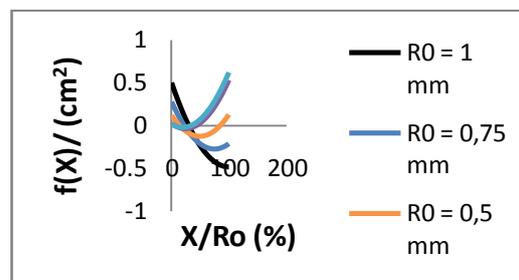
Figure3. *Extent for Fe^0 depletion (X/R$_0$) as function of the initial Fe^0 cylindrical particle radius (R$_0$ values). Working conditions: V$_{system}$ = 1.0 L, initial porosity (Φ$_0$) = 36 %, η= 2.08 and τ_{Fe}^0 = 1.*

Table3: *Fe^0 depletion as function of Fe^0 initial particle size (R$_0$). X values read from the Excel table for Fig.3*

D$_0$	R$_0$	R	X	P$_R$(%)	P$_C$(%)
(mm)	(mm)	(mm)	(%)	(mm)	(%)
2.00	1.00	0.70	30.00	9.00	91.00
1.50	0.75	0.52	23.00	5.29	94.71
1.00	0.50	0.35	15.00	2.25	97.75
0.50	0.25	0.18	7.00	0.49	99.51
0.40	0.20	0.14	6.00	0.36	99.64

Five different value of R$_0$ of cylindrical particles with less than 1.0 mm are used to show the evolution of f(X) as function of X/R$_0$ (in%). the volumetric proportion of iron τ_{Fe}^0 = 1. using Eq. (5) can be use to evaluate the extend of radius loss before clogging. Fig. 3 and Table 3 clearly shows that for the system with R$_0$ = 0.5 mm, R$_0$ = 0.25 mm, R$_0$ = 0.2 mm Eq. (5) has two solution. But physically only one solution is valid because it should less than the solution of Eq. 5 in case R$_0$=0.2 mm. Since pore spaces decrease with R$_0$, the extent of R$_0$ depletion is lower for the system with R$_0$ = 0.5 mm than for the system with R$_0$ = 0.25 mm. Fig. 3 shows sustainable Fe^0 filters for larger particules with comparably low reactivity. The introduction of nano-scale Fe^0 materials [53] find a explanation in this observation.

The results of table 3 suggest that for R$_0$ = 1.00mm, clogging occurs when a radius depletion of 91.00 % is achieved. Table 3 also suggests that for R$_0$ = 0.75mm, 94.71 % of radius depletion is this time achieved. In the first

case 0.3 mm will remain in the system versus 0.23 in the second case because of lack of space for expansive corrosion. These results clearly demonstrated that nano-scale Fe^0 materials should be admixing with non expansive matrixes. However, guideline of the application of nano-Fe^0 is yet to be developed. It should suggest a size of nano- Fe^0 which should be dispersed in a volume of not expansive material.

Permeability Loss in Fe^0 Filters

Fe^0 filters have been presented a universal solution for water treatment since 2009 [33]. However, the volumetric expansive iron corrosion is shown in this study as the major cause of permeability loss in Fe^0 filters. This factor have been mistakenly considered after the impact of gas production and foreign precipitates (e.g. CaCO$_3$) [1,6]. There is currently no agreement on the relative importance of these three major clogging factors. The accumulation of removed contaminants is intentionally neglected. Henderson and Demond [25] concluded that gas accumulation is the

major clogging factor. This study will undoubtedly improve their discussion. The calculations in this study documented the principal importance of expansive iron corrosion for the process of permeability loss. At $R_0 = 1.00$ mm, the porosity of the system is V_{pore}, at t_1 the porosity of the system evolutes to $V_{pore} = 0$, when corrosion stops because of lack of room for expansive iron dissolution. The scientific basis provided in this work will help for proper system design and evaluation. Equilibrium thermodynamics on the system between the initial stage and finalis considered when developing mathematic equation.

CONCLUDING REMARKS

In this work, a new universal equation of Fe^0 filters is provided given X as a function of the initial radius R_0, the initial volume of Fe^0, the initial porosity of the filter and the coefficient of volumetric expansion (O$_2$ availability). These different relevant parameters analyzed demonstrated that iron oxidation into Fe^{0}system strongly influence the process of permeability loss and thus its sustainability. The results also approve that sustainable filters should enclose less than 53% Fe^0 (vol/vol) and preferentially operate under oxic conditions. If a system must operate for a long period of time, results further reveal that too small Fe^0 particles should be promote. modeling the evolution of the hydraulic conductivity in engineered Fe^0 filters should be improve by using expression of the radius loss of individual reactive particles provided in this work.

REFERENCES

[1] M.A. Rahman, S. Karmakar, H. Salama, N. Gactha-Bandjun, B.D. Btatkeu-K., C. Noubactep Optimising the design of Fe^0-based filtration systems for water treatment: The suitability of porous iron composites, Journal of Solution Chemistry and Modeling2 (2013) 165–177.

[2] I. Ali, Water treatment by adsorption columns: Evaluation at ground level, Separation & Purification Reviews 43 (2014) 175–205.

[3] J.T. Cookson, Removal of submicron particles in packed beds, Environmental Science & Technology 4 (1970) 128–134.

[4] M. Zielina, Particle shapes in the drinking water filtration process, CLEAN – Soil, Air, Water 39 (2011) 941–946.

[5] Z. You, Y. Osipov, P. Bedrikovetsky, L. Kuzmina, Asymptotic model for deep bed filtration, Chemical Engineering Journal 258 (2014) 374–385.

[6] S. Caré, R. Crane, P.S. Calabro, A. Ghauch, E. Temgoua, C. Noubactep, Modelling the permeability loss of metallic iron water filtration systems, Clean – Soil, Air, Water 41 (2013) 275–282.

[7] R.W. Gillham, S.F. O'Hannesin, Enhanced degradation of halogenated aliphatics by zero-valent iron, Ground Water 32 (1994) 958–967.

[8] S.F. O'Hannesin, R.W. Gillham, Long-term performance of an in situ "Iron Wall" for remediation of VOCs, Ground Water 36 (1998) 164–170.

[9] D.H. Phillips, T. Van Nooten, L. Bastiaens, M.I. Russell, K. Dickson, S. Plant, J.M.E. Ahad, T. Newton, T. Elliot, R.M. Kalin, Ten year performance evaluation of a field-scale zero-valent iron permeable reactive barrier installed to remediate trichloroethene contaminated groundwater, Environmental Science & Technology 44 (2010) 3861–3869.

[10] R.T. Wilkin, S.D. Acree, R.R. Ross, R.W. Puls, T.R. Lee, L.L. Woods, Fifteen-year assessment of a permeable reactive barrier for treatment of chromate and trichloroethylene in groundwater, Science of the Total Environment 468–469 (2014) 186–194.

[11] C. Noubactep, Flaws in the design of Fe(0)-based filtration systems? Chemosphere 117 (2014) 104–107.

[12] S. Ulsamer, A model to characterize the kinetics of dechlorination of tetrachloroethylene and trichloroethylene by a zero valent iron permeable reactive barrier. Master thesis, Worcester Polytechnic Institute (2011) 73 pp.

[13] A.S. Ruhl, N. Ünal, M. Jekel, Evaluation of two-component Fe(0) fixed bed filters with porous materials for reductive dechlorination, Chemical Engineering Journal 209 (2012) 401–406.

[14] N.B. Pilling, R.E. Bedworth, The oxidation of metals at high temperatures, Journal of the Institute of Metals 29 (1923) 529–591.

[15] S. Caré, Q.T. Nguyen, V. L'Hostis, Y. Berthaud, Mechanical properties of the rustlayer induced by impressed current method in reinforced mortar, Cement and Concrete Research 38 (2008) 1079–1091.

[16] C. Noubactep, S. Caré, Dimensioning metallic iron beds for efficient contaminant removal, Chemical Engineering Journal 163 (2010) 454–460.

[17] C. Noubactep, S. Caré, F. Togue-Kamga, A. Schöner, P. Woafo, Extending service life of household water filters by mixing metallic iron with sand, Clean – Soil, Air, Water 38 (2010) 951–959.

[18] K. Miyajima, Optimizing the design of metallic iron filters for water treatment, Freiberg Online Geoscience 32 (2012) 60 pp.

[19] B.D. Btatkeu-K., H. Olvera-Vargas, J.B. Tchatchueng, C. Noubactep, S. Caré, Determining the optimum Fe0 ratio for sustainable granular Fe0/sand water filters, Chemical Engineering Journal 247 (2014) 265–274.

[20] D.D.J. Antia, Groundwater water remediation by static diffusion using nano-zero valent metals (Fe0, Cu0, Al0), n-FeHn+, n-Fe(OH)x, n-FeOOH, n-Fe-[OxHy](n+/-), In "Nanomaterials for Environmental Protection" Kharisov B.I., Kharissova O.V., Rasika Dias H.V. (Eds) (2014) 1–25, doi: 10.1002/9781118845530.ch1.

[21] Y. Bernabé, M. Zamora, M. Li, A. Maineult, Y.B. Tang, Pore connectivity, permeability, and electrical formation factor: A new model and comparison to experimental data, Journal of Geophysical Research: Solid Earth 116 (2011) B11204, doi:10.1029/2011JB008543.

[22] P.D.Mackenzie, D.P.Horney, M.T.Sivavec, Mineral precipitation and porosity losses in granular iron columns, Journal of Hazardous Materials 68(1999) 1–17.

[23] P. Westerhoff, J. James, Nitrate removal in zero-valent iron packed columns, Water Research 37 (2003) 1818–1830.

[24] R.L. Johnson, R.B. Thoms, R.O'B. Johnson, T. Krug, Field evidence for flow reduction through a zero-valent iron permeable reactive barrier, Ground Water Monitoring and Remediation 28 (2008) 47–55.

[25] A.D. Henderson, A.H. Demond, Impact of solids formation and gas production on the permeability of ZVI PRBs, Journal of Environmental Engineering 137 (2011) 689–696.

[26] R. Firdous, J.F. Devlin, Consideration of grain packing in granular iron treatability studies, Journal of Contaminant Hydrology164 (2014) 230–239.

[27] A.D. Henderson, A.H. Demond, Permeability of iron sulfide (FeS)-based materials for groundwater remediation, Water Research 47 (2013) 1267–1276.

[28] M.A. Keane, The removal of copper and nickel from aqueous solution using y zeolite ion exchangers, Colloids and Surfaces A: Physicochemical and Engineering Aspects 138 (1998) 11–20.

[29] J.B. Thibodeau, B. Chabot, C. Daneault, Calcium ion removal by a synthetic zeolite in the manufacture of mechanical grade papers, Pulp & Paper Canada 106 (2005) T71-74.

[30] W. Zhang, C.B. Wang, H.L. Lien, Treatment of chlorinated organic contaminants with nanoscale bimetallic particles, Catalysis Today 40 (1998) 387–395.

[31] C. Noubactep, A. Schöner, P. Woafo, Metallic iron filters for universal access to safe drinking water, Clean: Soil, Air, Water 37 (2009) 930–937.

[32] D.I. Kaplan, T.J. Gilmore, Zero-valent iron removal rates of aqueous Cr(VI) measured under flow conditions, Water, Air and Soil Pollution 155 (2004) 21–33.

[33] K. Kaczmarski, J.Ch. Bellot, Effect of particle-size distribution and particle porosity changes on mass-transfer kinetics, ActaChromatographica 13 (2003) 22–37.

[34] A.S. Ruhl, G. Franz, U. Gernert, M. Jekel, Corrosion product and precipitate distribution in two-component Fe(0) permeable reactive barriers, Chemical Engineering Journal 239 (2014) 26–32.

[35] R.Domga, F.Togue-Kamga, C.Noubactep, J.B. Tchatchueng, Discussing porosity loss of Fe^0 packed water filters at ground level. Chemical Engineering Journal 263 (2015) 127–134.

[36] TogueKamga F., Noubactep, C., and Woafo P., Modelling and simulation of iron/sand filter. Revue des sciences de l'eau, 25, 95, (2012).