Enhancing the sustainability of household Fe\textsuperscript{0}/sand filters by using bimetallics and MnO\textsubscript{2}.

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Abstract

Filtration systems containing metallic iron as reactive medium (Fe\textsuperscript{0} beds) have been intensively used for water treatment during the last two decades. The sustainability of Fe\textsuperscript{0} beds is severely confined by two major factors: (i) reactivity loss as result of the formation of an oxide scale on Fe\textsuperscript{0}, and (ii) permeability loss due to pore filling by generated iron corrosion products. Both factors are inherent to iron corrosion at pH > 4.5 and are common during the lifespan of a Fe\textsuperscript{0} bed. It is of great practical significance to improve the performance of Fe\textsuperscript{0} beds by properly addressing these key factors. Recent studies have shown that both reactivity loss and permeability loss could be addressed by mixing Fe\textsuperscript{0} and inert materials. For a non-porous additive like quartz, the threshold value for the Fe\textsuperscript{0} volumetric proportion is 51 %.

Using the Fe\textsuperscript{0}/quartz system as reference, this study theoretically discusses the possibility of (i) replacing Fe\textsuperscript{0} by bimetallic systems (e.g. Fe\textsuperscript{0}/Cu\textsuperscript{0}), or (ii) partially replacing quartz by a reactive metal oxide (MnO\textsubscript{2} or TiO\textsubscript{2}) to improve the efficiency of Fe\textsuperscript{0} beds. Results confirmed the suitability of both tools for sustaining Fe\textsuperscript{0} bed performance. It is shown that using a Fe\textsuperscript{0}:MnO\textsubscript{2} system with the volumetric proportion 51:49 will yield a filter with 40 % residual
porosity at Fe\textsuperscript{0} depletion (MnO\textsubscript{2} porosity 62 %). This study improves Fe\textsuperscript{0} bed design and can be considered as a basis for further refinement and detailed research for efficient Fe\textsuperscript{0} filters.

Keywords: Iron filters; Long-term reactivity; Oxide scale; Water treatment, Zerovalent iron.

1 Introduction

A filtration system containing metallic iron as reactive medium (hereafter termed as Fe\textsuperscript{0} bed) is an attractive method which can continuously remove contaminants from surface water, groundwater, and industrial effluent. The technology was introduced around 1990 by Canadian hydrogeologists [1-3]. The Fe\textsuperscript{0} bed technology has the potential to produce safe drinking water in water plants [4-6], and to treat wastewater [4,7-9] and groundwater [3,10,11]. Drawbacks for this innovative technology include (i) the accumulation of reaction by-products, (ii) the decrease in surface activity over time (reactivity loss), and (iii) the decrease of the bed permeability over the time (permeability loss) [11,12]. If Fe\textsuperscript{0} beds are used for above ground safe drinking water production, none of these three drawbacks is really a problem. In fact, individual beds will be replaced as soon as a problem is observed.

Fe\textsuperscript{0} beds have been demonstrated and used as an efficient and affordable technology for safe drinking water production at small scale (household and small community) [13-21]. The first generation filters made up of a 100 % layer of Fe\textsuperscript{0} were very efficient but not sustainable because of too rapid clogging [13,16]. The second generation filters used Fe\textsuperscript{0} and inert filling materials (mostly sand) and could achieve certain sustainability [19,22,23]. Recently, a theoretical discussion on the proportion of Fe\textsuperscript{0} in Fe\textsuperscript{0} beds has been performed [24-26]. Results demonstrated that the Fe\textsuperscript{0} volumetric ratio for sustainable filters is ≤ 52 % when the additive is non porous (e.g. quartz). This threshold value does not give any information on the nature of Fe\textsuperscript{0} (e.g. bimetallic, composite). The nature of filling materials has been discussed on the porosity perspective [25]. It is of great practical value to improve the performance of Fe\textsuperscript{0} beds. The following three perspectives could be addressed: (i) developing reliable Fe\textsuperscript{0}
materials (including composites), (ii) selecting the most suitable additive (porous, inert or/and reactive), and (iii) optimizing Fe$^0$ bed design (e.g. thickness of a bed).

The suitability of plated metal (bimetallic systems) for reactivity enhancement has already been demonstrated [27-29]. By plating a Fe$^0$ material with a more noble metal, the number of micro-defects in the crystal lattice due to different dimensions and charges of micro-alloyed elements, related to Fe$^0$ increase. Micro-alloyed components generate defects in a metal structure (interstitials and vacancies in crystal lattice) and an imbalance in the charge distribution, as a result of many micro-galvanic cells. These defects decrease energy barriers for transport of Fe$^{2+}$ ion from metal to oxide layer [27]. A positive accompanying effect is an increase in ionic and electronic conductivity and thus, an increase of corrosion rate ([27] and ref. cited therein). This makes the plated Fe$^0$ chemically much more reactive than the original Fe$^0$ material. Contaminant removal by bimetallic systems is based on several physico-chemical processes and the in situ formation of very reactive iron hydroxides. The major processes in a Fe$^0$ bed are adsorption, co-precipitation and size exclusion.

The ability of MnO$_2$ to sustain contaminant removal by Fe$^0$ was indirectly demonstrated in a recent study by He and Hering [30]. The authors demonstrated that As$^{\text{III}}$ was quantitatively oxidized to As$^{\text{V}}$ by MnO$_2$ but resulted As$^{\text{V}}$ remained in solution. Quantitative As removal was indeed observed in systems containing Fe$^{\text{II}}$ and was mostly attributed to As co-precipitation with Fe$^{\text{III}}$ hydroxides. In a similar way, MnO$_2$ can sustain Fe$^0$ oxidative dissolution yielding Fe$^{\text{II}}$ which capability to induce reductive dissolution of MnO$_2$ will sustain the process of contaminant removal. Note that the work of He and Hering [30] recalled that “contaminant reduction” and “contaminant removal” should never be randomly interchanged. In other words, a chemical transformation (oxidation or reduction) may favour contaminant removal but is not a stand alone removal mechanism. Aqueous contaminant removal by co-precipitation with in-situ generated metal hydroxides is well documented process for all classes of contaminants ([29, 31] and ref. therein).
The present study intends to theoretically discuss the optimization of Fe\textsuperscript{0} bed by two different tools: (i) replacing Fe\textsuperscript{0} by a bimetallic system, and (ii) using MnO\textsubscript{2} as reactive additives, e.g. partially or totally substituting quartz by MnO\textsubscript{2} in a reference Fe\textsuperscript{0}/quartz bed. Both tools have the potential to improve the contaminant removal efficiency and prolong the lifespan of Fe\textsuperscript{0} beds. For the sake of clarity, the process of contaminant removal in Fe\textsuperscript{0} beds will be first presented.

2 Contaminant removal in Fe\textsuperscript{0} filters

2.1 Filtration in packed-column

A Fe\textsuperscript{0} bed is primarily a packed-column of granular Fe\textsuperscript{0} and quartz (sand) particles. The efficiency of packed-columns for contaminant removal is usually evaluated by monitoring the time dependent evolution of (i) the contaminant concentration in the effluent, and (ii) the water velocity through the column. Physical and chemical conditions evaluated in such experiments include grain particle size and shape, solution pH, solution ionic strength and composition [32,33]. Ideally, contaminants are deposited throughout the entire filter media. Accordingly, Fe\textsuperscript{0} filtration is a deep-bed or depth filtration process [34].

2.2 Filtration in a Fe\textsuperscript{0} bed

Contaminant removal within a Fe\textsuperscript{0}/quartz filter is not comparable to contaminant removal by an adsorption column [5,35]. The most important feature of Fe\textsuperscript{0}/quartz filters regards the specificity of the removal process. In an adsorption column, contaminants with different physico-chemical properties can be separated due to their differential affinity to the adsorbing material (e.g. activated carbon, iron oxide). Similarly, particles with different sizes can be separated in a depth sand filter. But in a Fe\textsuperscript{0}/quartz filter, there is primarily no such specificity as contaminants are removed during the dynamic process of iron corrosion products formation (Fe hydroxides/oxides) and by resulted Fe hydroxides/oxides [35, 36].

2.3 Mechanism of contaminant removal in Fe\textsuperscript{0}/sand filters
Regardless from any contaminant inflow, the initial pore space in a Fe\(^0\)/quartz filter is progressively filled by in situ generated Fe hydroxides/oxides. Decreased pore space is coupled to improved size exclusion capacity. Accordingly, regardless from physico-chemical interactions between contaminants, Fe\(^0\) and Fe hydroxides/oxides, contaminant removal by pure size exclusion will inevitably occur with increasing service life. This fundamental aspect has received little attention to date as the scientific community was focused on specific interactions between selected contaminants and Fe\(^0\). In this effort a particular attention was paid to chemical reduction [10,11].

It has already been demonstrated that contaminants are fundamentally entrapped within the film of corrosion products in the vicinity of the Fe\(^0\) surface [37-40]. It is essential to note that the formation of corrosion products is a cycle of expansion/contraction occurring in the pore space [5,26,35]. During this process, native iron (Fe\(^0\): SSA < 1 m\(^2\)/g) is first transformed to voluminous iron hydroxides possibly having specific surface area (SSA) > 500 m\(^2\)/g before progressively contracted to amorphous and crystalline oxides with SSA \(\leq 10\) m\(^2\)/g. The voluminous colloid which is intermediary formed [41] during an expansion/contraction cycle can be compared to a spider web which traps inflowing contaminants and keeps them adsorbed while the colloid is further transformed. In other words, before the pore space becomes close enough for the Fe\(^0\) filter to act as an ultra-filtration system, the expansion/contraction cycle traps contaminants from the infiltrating water. It is certain, that the kinetics of iron oxidation will decrease as soon as not enough space is available for expansive corrosion. This is a plausible explanation for the controversial observation, that TCE removal rates were higher in a system with 85 % Fe\(^0\) than they were in a 100 % Fe\(^0\) (w/w) system [42]. Substituting a fraction of Fe\(^0\) by sand (quartz) was proven a prerequisite for efficient long-term permeable Fe\(^0\) filters [24,25]. The present study aims at theoretically discussing the substitution of a portion of quartz in the dual media (Fe\(^0\)/quartz) by a reactive...
oxide to sustain long-term Fe$^0$ reactivity. A further discussed way to sustain Fe$^0$ reactivity is to plate Fe$^0$ by a second more electropositive metal.

3  
Sustaining Fe$^0$ reactivity

The presentation above has suggested that successful contaminant removal in a Fe$^0$/quartz bed is coupled with the whole process of iron corrosion. Accordingly, a reliable way to warrant continuous contaminant removal is to sustain iron corrosion. This section examines two possibilities of sustaining Fe$^0$ corrosion.

3.1  Use of bimetallics

The deposition of small amounts of second metals such as Ni and Pd onto the Fe$^0$ surface has been proven beneficial for the process of aqueous contaminant removal ([12] and ref. therein). Bimetallic systems are an efficient media for accelerating the decontamination [27-29]. The prevailing operating mode of bimetallic systems [12] was recently challenged. It was shown that any enhanced contaminant reduction, if applicable, occurs by an indirect process [43]. Table 1 summarises the standard electrode potentials of seven elemental metals (Me$^0$) which may be used to sustain Fe$^0$ oxidation in filters: Co$^0$, Ni$^0$, Cu$^0$, Ag$^0$, Pd$^0$, Pt$^0$, Au$^0$. From these metals, Cu$^0$ is the most used.

An ideal Me$^0$ acts as a catalyst. For example, Cu$^0$ is oxidized by water to Cu$^{2+}$ and the resulted Cu$^{2+}$ oxidizes Fe$^0$. Considering Me$^0$ as pure catalyst, calculated amounts of Fe$^0$/Me$^0$ will be added to a sand filter and the porosity will vary as in a Fe$^0$/quartz bed. In other words, replacing Fe$^0$ particles by bimetallic (Fe$^0$/Me$^0$) particles of similar size and occupying the same volume will not significantly impact porosity loss. Bimetallic/quartz filters will behave like Fe$^0$/quartz filters in term of the evolution of the porosity but exhibit an enhanced long-term reactivity. The theoretical evolution of porosity loss due to clogging is discussed in section 4.

3.2  Use of metal oxides
The use of natural oxides to sustain Fe\(^0\) reactivity was derived from the well-documented reductive dissolution of MnO\(_2\) by Fe\(^{II}\) [46,47]. This process was successfully used to demonstrate the importance of corrosion products in the process of contaminant removal by Fe\(^0\) [48-52]. Moreover, the reductive dissolution of MnO\(_2\) by Fe\(^{II}\) is a well-established hydrometallurgical process [53-55]. Recently, Bafghi et al. [55] published a work on the reductive dissolution of manganese ore in the presence of Fe\(^0\). Based on theoretical and experimental facts, they concluded that Fe\(^0\) was superior to Fe\(^{II}\) for MnO\(_2\) reductive dissolution. However, they insisted on the fact that Fe\(^{II}\) is more available. Mechanistic details will not be considered here as it is sufficient to consider that metal oxides could sustain Fe\(^0\) corrosion (Tab. 2, Tab. 3). Remember that contaminants are fundamentally removed by iron corrosion products (adsorption and co-precipitation) and these are increasingly available when iron oxidation is sustained by Fe\(^{II}\) consumption [51,52,56].

Only the four naturally abundant oxides will be considered: Al\(_2\)O\(_3\), MnO\(_2\), SiO\(_2\) and TiO\(_2\) (Tab. 2). The standard electrode potentials from Tab. 2 show that only MnO\(_2\) and TiO\(_2\) could sustain Fe\(^0\) reactivity. Accordingly, Al\(_2\)O\(_3\) and SiO\(_2\) can only be used as inert filling materials. The ability of MnO\(_2\) to sustain Fe\(^0\) corrosion was already demonstrated [48-50,56]. In particular, the success of SONO Arsenic Filters in Bangladesh is based on continuous production of reactive iron oxides by the used manganese oxide/Fe\(^0\) composite (coupled to size exclusion in the filter). Table 3 depicts some relevant electrode reactions (half-reactions) for the discussion of the Fe\(^0\) reactivity. From Tab. 3 it can be seen that MnO\(_2\) is theoretically by far superior to TiO\(_2\) in sustaining Fe\(^0\) corrosion. However, the suitability of available metal oxides to sustain Fe reactivity should be tested on a case-by-case basis. Moreover, the objective should not be to use the most reactive metal oxide but rather the one with satisfactorily reactivity for individual purposes. For example, for a given Fe\(^0\), a very reactive MnO\(_2\) can accelerate the Fe\(^0\) corrosion in such a way that filter fouling/clogging is achieved similar as with bio-corrosion [10,11]. In such situations a lesser reactive MnO\(_2\) should be
used. Testing well-characterized Fe$^0$ and reactive manganese oxides in various proportions is regarded as a tool to produce site-specific composites. In fact, the composite currently used in SAF filters is the same material which is used everywhere (actually mostly in Bangladesh and Nepal) [14,18]. However, contaminated waters are of various background compositions and each water could be treated with appropriate composites.

To discuss the evolution of the pore space within the filter as metal oxides react, it will be considered that MnO$_2$ and TiO$_2$ reduction at neutral pH values mostly yield insoluble hydroxides: MnOOH and TiOOH (Eq. 17 and Eq. 18).

\[
\begin{align*}
\text{Fe}^0 + 3 \text{MnO}_2 + 2 \text{H}_2\text{O} & \rightleftharpoons \text{FeOOH} + 3 \text{MnOOH} & (17) \\
\text{Fe}^0 + 3 \text{TiO}_2 + 2 \text{H}_2\text{O} & \rightleftharpoons \text{FeOOH} + 3 \text{TiOOH} & (18)
\end{align*}
\]

Eq. 17 and 18 suggest that the oxidation of one Fe atom consumes three molecules of the adsorbent MnO$_2$ (or TiO$_2$) and produces one FeOOH and three MnOOH (or three TiOOH) as new adsorbents. The volume variation is estimated based on values of the specific weight defined as the ratio of the molecular volume of the reaction products to the molecular volume of the educts (Tab. A3). The discussion will only concern MnO$_2$ because no tabulated value could be found for TiOOH. The evolution of the porosity loss due to clogging is discussed in section 4.

4 Evolution of the residual porosity using bimetallic particles or metal oxides

This section will start with some general design equations. It has been recently showed that dimensionless design equations could be written such that for each practical case the appropriate values are derived [24-26]. In other words, the same equations are applied to household Fe$^0$ filters, Fe$^0$ treatment trench, and Fe$^0$ reactive walls. In each case, the used materials (Fe$^0$ and additives) should be thoroughly characterized. Relevant material characteristics include porosity, particle size, shape, specific weight, and surface area. The impacts of material characteristics on the bed efficiency are not discussed here.

4.1 General design equations of Fe$^0$ beds
Cylindrical beds are considered. H is the height and D is the internal diameter. The cylinder contains a reactive zone with the height $H_{rz}$ and the volume $V_{rz}$. Beds are supposed to be filled by granular materials. The compactness (or packing density) $C$ (-) is defined as the ratio of the volume of the particles to the total packing volume ($V_{rz}$). Considering the granular material as composed of mono-dispersed spheres subjected to soft vibrations, the compactness $C$ is generally considered to be equal to 0.64 for a random close packing. It is assumed that the particles are non-porous.

The initial porosity $\Phi_0$ (-) of the reactive zone and the thickness $H_{rz}$ of the reactive zone are respectively then given by:

$$\Phi_0 = 1 - C$$  \hspace{1cm} (19)

$$H_{rz} = \frac{4}{\pi D^2} \cdot V_{rz}$$  \hspace{1cm} (20)

The filling of the bed porosity by iron corrosion products can be estimated from a simplified modeling (Fig. 1) based on the following assumptions:

(i) uniform corrosion: the radius reduction of the spherical particles is the same for all the Fe$^0$ particles.

(ii) the packing density $C$ remains constant for all particles (Fe$^0$ and quartz). The volume of the granular material is not modified by the corrosion process: no pressure induced by rust formation around Fe particles and no compaction of the Fe$^0$ mixture during the corrosion process ($V_{rz}$ remains constant).

(iii) reaction products are fluid enough to progressively fill available pore space.

Assuming that the coefficient of volumetric expansion or the specific volume ($\eta$) of the reaction products is:

$$\eta = \frac{V_{\text{oxide}}}{V_{\text{Fe}}}$$  \hspace{1cm} (21)
where $V_{\text{oxide}}$ is the volume of the reaction product and $V_{\text{Fe}}$ the volume of the parent $\text{Fe}^0$. It is assumed that $\text{Fe}_3\text{O}_4$ is the sole iron corrosion product for the Fe/quartz system. The specific volume for $\text{Fe}_3\text{O}_4$ is 2.1.

The surplus volume of the reaction products contributing to porosity loss is $V'_{\text{oxide}}$. Per definition $V'_{\text{oxide}}$ is the difference between the volume $V_{\text{oxide}}$ of reaction products and the volume $V_{\text{Fe}}$ of parent $\text{Fe}^0$. $V'_{\text{oxide}}$ is given by Eq. 22:

$$V'_{\text{oxide}} = (\eta - 1) \cdot V_{\text{Fe}}$$  \hspace{1cm} (22)$$

Assuming that iron expansive corrosion is the sole clogging factor, the bed is clogged when the volume $V'_{\text{oxide}}$ is equal to the initial inter-granular voids ($\Phi_0, V_{\text{rz}}$), the volume $V_{\text{Fe,clogging}}$ of the consumed $\text{Fe}^0$ leading to clogging of the bed is then estimated by:

$$V_{\text{Fe,clogging}} = \frac{\Phi_0 \cdot V_{\text{rz}}}{\eta - 1}.$$  \hspace{1cm} (23)$$

Eq. 23 is of fundamental importance for $\text{Fe}^0$ bed design as it determines the ideal $\text{Fe}^0$ volume (and thus $\text{Fe}^0$ mass) to be used. If $V_0$ is the initial volume of dense $\text{Fe}^0$, three cases can be distinguished:

(i) $V_{\text{Fe,clogging}} > V_0$, no clogging due to expansive iron corrosion will occur. In this case, the real volume of Fe which may be consumed ($V_{\text{consumed-Fe}}$) is equal to the initial volume $V_0$ of Fe ($V_{\text{consumed-Fe}} = V_0 < V_{\text{Fe,clogging}}$) and there is a residual porosity at $\text{Fe}^0$ depletion ($\Phi_r \neq 0$);

(ii) $V_{\text{Fe,clogging}} = V_0$, clogging will not occur before $\text{Fe}^0$ depletion ($V_{\text{consumed-Fe}} = V_{\text{Fe,clogging}} = V_0$) but the final porosity is zero ($\Phi_r = 0$);

(iii) $V_{\text{Fe,clogging}} < V_0$, clogging will occur before $\text{Fe}^0$ depletion ($\Phi_r = 0$). In this case, the real volume of consumed Fe leading to clogging is inferior to the initial volume $V_0$ of Fe ($V_{\text{consumed-Fe}} = V_{\text{Fe,clogging}} < V_0$) and the excess $\text{Fe}^0$ amount should be regarded as pure material wastage [24]."
The residual porosity \( \Phi_r \) defined by \( \Phi_r = \frac{V_{\text{residual voids}}}{V_{rz}} \) and the residual mass of the iron (Fe\(^0\)) are evaluated by Eq. 24 and Eq. 25:

\[
\Phi_r = \Phi_0 - (\eta - 1) \cdot \frac{V_{\text{consumed-Fe}}}{V_{rz}} \quad (24)
\]

\[
\frac{M}{M_0} = \frac{V_0 - V_{\text{consumed-Fe}}}{V_0} \quad (25)
\]

where \( V_0 \) is the initial volume of Fe, \( V_{\text{consumed-Fe}} \) is the volume of the Fe which is consumed and \( M \) is the actual mass of Fe given by \( M = \rho_{Fe} \cdot (V_0 - V_{\text{consumed-Fe}}) \) with \( \rho_{Fe} = 7,800 \text{ kg/m}^3 \).

When the clogging appears before depletion of Fe\(^0\), the volume \( V_{\text{consumed-Fe}} \) is given by the Eq. 24 and the residual porosity is \( \Phi_r = 0 \) and there is a residual mass of iron \( M/M_0 \neq 0 \) (Eq. 25).

When there is no clogging, the volume \( V_{\text{consumed-Fe}} \leq V_0 \) and \( \Phi_r \neq 0 \) (Eq. 24) and the Fe\(^0\) mass at Fe\(^0\) depletion is zero (\( M/M_0 = 0 \); Eq. 25).

Eq. 19 through 25 should be routinely used to design laboratory experiments, pilot and field works.

4.2 Case of bimetallic/quartz system

To sustain the Fe\(^0\) reactivity, Fe particles are replaced by bimetallic particles of comparable particle sizes. For Fe\(^0\)/Cu\(^0\) bimetallic particles with 7% in mass of Cu, the volumetric proportion of Fe\(^0\) is 93.85% (considering for specific weights \( \rho_{Fe} = 7800 \text{ kg/m}^3 \) and \( \rho_{Cu} = 8960 \text{ kg/m}^3 \)) and the reaction product is Fe\(_3\)O\(_4\). The residual porosity and the residual mass are given by the same equations by replacing the initial volume \( V_0 \) of Fe\(^0\) by 93.85%* \( V_0 \). The results for the Fe\(^0\)/quartz and the bimetallic/quartz systems are given in Fig. 1. The trends are similar for both cases. While decreasing the Fe\(^0\) proportion at constant reactive zone thickness, Fe\(^0\) depletion was achieved for Fe\(^0\)/quartz systems > 51 vol-% Fe\(^0\). In the case of bimetallic/quartz system (Fe\(^0\)/Cu\(^0\)), the clogging is avoided for < 54 vol-% bimetallic.

To further sustain the efficiency of Fe\(^0\) beds, bimetallic systems containing larger amounts of plating metals (Me\(^0\)) could be used. Moreover composites should be manufactured and tested.
Those composites should contain uniformly distributed Me$^0$ in the bulk of Fe$^0$ materials and not just deposited at their surface. Apart from such bulk composites, special Fe$^0$ materials with higher contents in S for instance, could be manufactured and tested. In fact, during the steel making process, efforts target as completely remove S are made. Sulphur is known for its negative effect on corrosion resistance of steel. However, in the context of water treatment with Fe$^0$, readily corrosive Fe$^0$ may be suitable.

### 4.3.1 Case of Fe$^0$/MnO$_2$/quartz system

A reference reactive zone is considered as made up of 51 vol-% Fe$^0$ and 49 vol-% quartz as it allows avoiding the clogging before Fe$^0$ depletion as shown in Fig. 1. Iron filings from Gotthart Maier Metallpulver GmbH (Rheinfelden, Germany) containing 92 % Fe$^0$ (w/w) is used for the calculations. Quartz particles of similar particle size are replaced by MnO$_2$ particles in order to increase Fe$^0$ reactivity. In presence of MnO$_2$, it is assumed that chemical reactions yield to FeOOH and MnOOH products (Eq. 17). When MnO$_2$ particles have been consumed, the Fe corrosion process leads to the reaction products Fe$_3$O$_4$.

Calculations made with characteristics of a natural MnO$_2$ ($\phi_{MnO_2} = 62 \%$) given by Li et al. [57] are used in this study (Tab. A.1 and A.2). The mineral contained (weight) 77.8 % MnO$_2$, 2.7 % Fe, 0.87 % Si, 2.78 % Al and 0.01 % S. For simplifications, it is considered that the mineral is made up of 77.8 % MnO$_2$ and 22.2 % of a “gangue” having the characteristic of quartz (inert and non porous). This assumption was the rationale to use the specific weight of quartz in estimating the volumetric expansion coefficient for MnO$_2$ (Appendix). Calculations showed that for the reference system (vol. Fe:quartz = 51:49), less than 3 % Fe$^0$ is necessary to consume the amount of MnO$_2$ that could be contained in up to 49 vol-% MnO$_2$, when quartz is completely replaced by MnO$_2$. Moreover, it is shown that thanks to the porosity of MnO$_2$, there is a net increase of the initial bed porosity in comparison to the Fe$^0$/quartz bed. Furthermore, because the chemical transformation (Fe + MnO$_2$) to (MnOOH +FeOOH) was
not expansive but slightly compressive ($\eta = 0.94$), there is a net increase of the residual bed porosity (Appendix).

Eq. 24 and 25 are slightly modified because the initial porosity $\Phi_0$ is increased by the internal porosity of the MnO$_2$ particles and the voids ($\Phi_0, V_{rz}$) are filled by (i) the MnOOH hydroxides with $\eta_1 = V_{\text{MnOOH}}/V_{\text{MnO}_2} = 0.94$ (Appendix), (ii) the FeOOH hydroxides with $\eta_2 = V_{\text{FeOOH}}/V_{\text{Fe}} = 3.03$ and (iii) Fe$_3$O$_4$ with $\eta_3 = V_{\text{Fe}_3\text{O}_4}/V_{\text{Fe}} = 2.1$. Values of $\eta_2$ and $\eta_3$ are from ref. [58].

The initial porosity $\Phi_0$, the residual porosity $\Phi_r$ and the residual mass of the iron ($\text{Fe}^0$) are evaluated by Eq. 26, Eq. 27 and Eq. 28:

$$\Phi_0 = (1 - C) + f_{\text{MnO}_2} \cdot \Phi_{\text{MnO}_2}$$  \hspace{1cm} (26)

$$\Phi_r = \Phi_0 - \frac{(\eta_1 - 1) \cdot V_1 + (\eta_2 - 1) \cdot V_2 + (\eta_3 - 1) \cdot V_3}{V_{rz}}$$  \hspace{1cm} (27)

$$\frac{M}{M_0} = \frac{V_0 - V_2 - V_3}{V_0}$$  \hspace{1cm} (28)

Where $\Phi_{\text{MnO}_2}$ is the internal porosity of the MnO$_2$ particles ($\Phi_{\text{MnO}_2} = 62\%$) and $f_{pp}$ (-) is the porous particle volume fraction determined by $f_{pp} = V_{\text{MnO}_2}/V_{\text{MnO}_2}$ with $V_{\text{MnO}_2}$ the volume of the porous particles MnO$_2$. $V_1$ is the volume of the dense MnO$_2$, $V_2$ is the $\text{Fe}^0$ volume which reacts with MnO$_2$. The volume of $\text{Fe}^0$ ($V_2$) is obtained considering that one Fe atom consumes three molecules of MnO$_2$ (Eq. 17). $V_3$ is the volume of $\text{Fe}^0$ leading to Fe$_3$O$_4$ after MnO$_2$ depletion.

At Fe depletion ($M/M_0 = 0$), the residual porosity $\Phi_r$ is given by Eq. 27 ($V_3 = V_0 - V_2$ with $V_0$ the initial volume of $\text{Fe}^0$ in the reactive zone). If clogging appears before depletion of $\text{Fe}^0$, the residual porosity is $\Phi_r = 0$ and the residual mass is given by Eq. 28.

The evolution of the initial and residual porosity is given in Fig. 2a for the reference system when the volumetric proportion of MnO$_2$ varies from 0 to 49 %. Thanks to the internal porosity of MnO$_2$ the initial porosity ($\Phi_0$) increased from 36.0 to 55.4 %. On the other hand,
Fe\textsuperscript{0} depletion was observed in all systems but the residual porosity varies from 8.3 to 40.6 %.

The increase of the residual porosity with increasing MnO\textsubscript{2} proportion is due to two factors: (i) the internal porosity of MnO\textsubscript{2} and (ii) the light volumetric compaction of MnO\textsubscript{2} reduction to MnOOH. Remember that in the reference system the residual porosity is zero at Fe\textsuperscript{0} depletion. Therefore, similarly as for the Fe\textsuperscript{0}/pumice system [25,59], the internal porosity of MnO\textsubscript{2} could be regarded as storage room for in situ generated corrosion products (see also Appendix). In summary, MnO\textsubscript{2} reduction to MnOOH has two beneficial effects: (i) sustaining Fe\textsuperscript{0} reactivity and (ii) serving as storage room for corrosion products. Additionally, the chemical potential of the reaction between Fe\textsuperscript{II} and MnO\textsubscript{2} will drive the diffusion of Fe\textsuperscript{II} from Fe\textsuperscript{0} oxidative dissolution to the internal surface of MnO\textsubscript{2}. Thus, filling the internal porosity of MnO\textsubscript{2} with iron corrosion products is more likely to occur than for an inert material like pumice. Another important aspect is that Mn\textsuperscript{II} from the reductive dissolution of MnO\textsubscript{2} will migrate in the system and be oxidized by several species to MnOOH or MnO\textsubscript{2} [60-62] which will further oxidize Fe\textsuperscript{II} from Fe\textsuperscript{0}. Accordingly, despite stoichiometric disadvantage, MnO\textsubscript{2} may work as catalyst to sustain Fe\textsuperscript{0} reactivity during its whole lifespan [63,64].

The fact that no pore clogging was observed for 51 vol-% Fe\textsuperscript{0} suggests that more Fe\textsuperscript{0} could be used for the same bed (V\textsubscript{w} constant). In this case, the volume of MnO\textsubscript{2} is necessarily reduced. Fig. 2b shows the results of systems with volumetric ratios Fe\textsuperscript{0}:MnO\textsubscript{2} varying between 60:0 and 60:40. That is, when quartz is progressively replaced by MnO\textsubscript{2}. While the initial porosity increased from 36 to 51.9 %, the residual porosity increased from 0.0 to 24.8 %. This results show clearly that even in rising the Fe\textsuperscript{0} volumetric ratio in the column from 51 to 60 %, a residual porosity exists and the Fe\textsuperscript{0} performance is increased by the cycle of MnO\textsubscript{2} as described above.

5 Concluding remarks

A Fe\textsuperscript{0}/quartz filter is regarded as an assisted slow sand filtration system which efficiency is improved by addition of a calculated amount of metallic iron [65]. The aqueous corrosion by
infiltrating raw water should ideally transform the initial Fe\(^0\) filter to an efficient filtration system. Improved filtration efficiency is based on the volumetric expansive nature of iron corrosion [59,66] which ideally only partly fills initial pore space in the sand-like filter [67].

This communication is part of an ongoing effort for low-cost water treatment using well-designed Fe\(^0\) beds [5,6,17,24-26,68,69]. While dual filters of Fe\(^0\) and quartz will be long-term permeable, the substitution of Fe\(^0\) by bimetallic materials or the substitution of inert sand by reactive metal oxides will sustain long-term reactivity. For example, sustaining Fe\(^0\) reactivity by substituting a fraction of Fe\(^0\) by metallic copper chips or (partly or entirely) replacing sand by granulated MnO\(_2\) will help to design efficient and sustainable filtration systems. The encouraging results of SONO filters in Bangladesh [14,15,18,70-72] suggest that practitioners of subsurface permeable barriers should check the possibility of replacing Fe\(^0\) by composites or amended Fe\(^0\) by reactive additives. The concept presented and discussed in this communication (and related articles) would be useful in designing efficient and affordable water filtration systems at several scales. The concept also renders itself as a basis for further refinement and detailed research at laboratory and field scale. One may wonder how the Fe\(^0\) bed technology will be developed in different parts of the world.

Acknowledgments

Dr. Boniface P. T. Fokwa (Institute of Inorganic Chemistry, RWTH Aachen University) is acknowledged for fruitful discussions on the mineralogy of manganese oxides. The manuscript was improved by the insightful comments of anonymous reviewers from CLEAN Soil, Air, Water.

References


Table 1: Relevant half-reactions for more electropositive metals likely to be added to sustain iron corrosion in household filters with the relevant standard electrode potentials. Standard electrode potentials are arranged in increasing order of $E^\circ$. The higher the $E^\circ$ value, the stronger the oxidative capacity for $Fe^0$. Standard electrode potentials are compiled from refs. [44,45].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^\circ$ (V)</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fe^{2+} + 2 e^- \rightleftharpoons Fe^0$</td>
<td>-0.44</td>
<td>(1)</td>
</tr>
<tr>
<td>$Co^{2+} + 2 e^- \rightleftharpoons Co^0$</td>
<td>-0.28</td>
<td>(2)</td>
</tr>
<tr>
<td>$Ni^{2+} + 2 e^- \rightleftharpoons Ni^0$</td>
<td>-0.24</td>
<td>(3)</td>
</tr>
<tr>
<td>$Cu^{2+} + 2 e^- \rightleftharpoons Cu^0$</td>
<td>0.33</td>
<td>(4)</td>
</tr>
<tr>
<td>$Ag^{+} + e^- \rightleftharpoons Ag^0$</td>
<td>0.80</td>
<td>(5)</td>
</tr>
<tr>
<td>$Pd^{2+} + 2 e^- \rightleftharpoons Pd^0$</td>
<td>0.95</td>
<td>(6)</td>
</tr>
<tr>
<td>$Pt^{2+} + 2 e^- \rightleftharpoons Pt^0$</td>
<td>1.18</td>
<td>(7)</td>
</tr>
<tr>
<td>$Au^{3+} + 3 e^- \rightleftharpoons Au^0$</td>
<td>1.50</td>
<td>(8)</td>
</tr>
</tbody>
</table>
Table 2: Inventory of possible redox couples in the present study with the relevant standard electrode potentials. Standard electrode potentials are compiled from ref. [56,57]. (*) marked are values from wikipedia. Relevant redox couples are those which could oxidize Fe⁰ (E⁰ > -0.44 V). Accordingly, only MnO₂ and TiO₂ are relevant.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Species</th>
<th>Couples</th>
<th>E⁰</th>
<th>Relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(V)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Al⁰, Al³⁺</td>
<td>Al³⁺/Al⁰</td>
<td>-1.67</td>
<td>No</td>
</tr>
<tr>
<td>MnO₂</td>
<td>Mn⁰, Mn²⁺, Mn³⁺, Mn⁴⁺</td>
<td>Mn²⁺/Mn⁰</td>
<td>-1.18</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn³⁺/Mn²⁺</td>
<td>1.54</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn⁴⁺/Mn²⁺</td>
<td>1.23</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn⁴⁺/Mn³⁺</td>
<td>0.95(*)</td>
<td>Yes</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Si⁰, Si⁴⁺</td>
<td>Si⁴⁺/Si⁰</td>
<td>-0.99</td>
<td>No</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Ti⁰, Ti³⁺, Ti⁴⁺</td>
<td>Ti³⁺/Ti⁰</td>
<td>-1.63(*)</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti⁴⁺/Ti³⁺</td>
<td>0.19(*)</td>
<td>Yes</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Fe⁰, Fe²⁺, Fe³⁺</td>
<td>Fe²⁺/Fe⁰</td>
<td>-0.44</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe³⁺/Fe²⁺</td>
<td>0.77</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Table 3: Relevant half-reactions for sustaining iron corrosion with the relevant standard electrode potentials. Standard electrode potentials are arranged in increasing order of $E^0$. The higher the $E^0$ value, the stronger the oxidative capacity for $\text{Fe}^0$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0$ (V)</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{2+} + 2 \text{e}^- \Leftrightarrow \text{Fe}^0$</td>
<td>-0.44</td>
<td>(9)</td>
</tr>
<tr>
<td>$2 \text{H}^+ + 2 \text{e}^- \Leftrightarrow \text{H}_2 (g)$</td>
<td>0.00</td>
<td>(10)</td>
</tr>
<tr>
<td>$\text{TiO}_2(s) + 4 \text{H}^+ + \text{e}^- \Leftrightarrow \text{Ti}^{3+} + 2 \text{H}_2\text{O}$</td>
<td>0.19</td>
<td>(11)</td>
</tr>
<tr>
<td>$\text{Fe}^{3+} + \text{e}^- \Leftrightarrow \text{Fe}^{2+}$</td>
<td>0.77</td>
<td>(12)</td>
</tr>
<tr>
<td>$\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \Leftrightarrow 4 \text{OH}^-$</td>
<td>0.81</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{MnO}_2(s) + 4 \text{H}^+ + \text{e}^- \Leftrightarrow \text{Mn}^{3+} + 2 \text{H}_2\text{O}$</td>
<td>0.95</td>
<td>(14)</td>
</tr>
<tr>
<td>$\text{MnO}_2(s) + 4 \text{H}^+ + 2 \text{e}^- \Leftrightarrow \text{Mn}^{2+} + 2 \text{H}_2\text{O}$</td>
<td>1.23</td>
<td>(15)</td>
</tr>
<tr>
<td>$\text{MnOOH} (s) + 3\text{H}^+ + \text{e}^- \Leftrightarrow \text{Mn}^{2+} + 2 \text{H}_2\text{O}$</td>
<td>1.54</td>
<td>(16)</td>
</tr>
</tbody>
</table>
Figure 2:

(a) 51 vol-% Fe

(b) 60 vol-% Fe

\[ \text{porosity} / [\%] \]

\[ \text{MnO}_2 / [\text{vol-%}] \]

\[ \Phi_0 \]

\[ \Phi / \Phi_0 \]
Figure Captions

Figure 1: Evolution of the residual porosity $\Phi_r/\Phi_0$ (%) (a) and the residual mass of Fe$^0$ $M_r/M_0$ (%) (b) versus the volumetric % ratio of material in the Fe$^0$ bed. It is clear that in both cases, for Fe$^0 > 51$ vol-%, bed clogging will occur before Fe$^0$ depletion. For a 100 % Fe$^0$ bed, only 51 w-% of Fe$^0$ is consumed at bed clogging.

Figure 2: Evolution of the residual porosity versus the % replaced quartz particles by MnO$_2$ for 51 % Fe$^0$ (a) and 60 % Fe$^0$ (b). It is evident that replacing quartz by porous MnO$_2$ could enable the use of a larger amount of Fe$^0$ in a bed.
Appendix

A.1 Estimation of the $\eta$-value for MnOOH

Table A.1 summarizes relevant characteristics of selected manganese oxides and Tab. A.2 gives the volume and the ratio of the volume of MnOOH to other oxides [73,74]. Apart from MnOOH, all oxides listed in Tab. A.1 may be considered as potential starting materials.

The volumetric contraction or expansion coefficient $\eta$ expressed as the ratio of the volume of MnOOH to the volume of each oxide is determined according to:

$$\eta = \frac{V_{\text{MnOOH}}}{V_{\text{oxide}}} = \frac{(M_{\text{MnOOH}}/\rho_{\text{MnOOH}})}{(M_{\text{oxide}}/\rho_{\text{oxide}})}$$  
(S1)

With $M_i$ and $\rho_i$ the mass and specific weight of the i species (MnOOH or oxide)

As the mass of MnOOH and the oxides can be expressed by $M_i = M_z * n_i$ where $M_z$ is the molecular weight and $n_i$ is the number of mole of each species in the chemical reaction, the coefficient $\eta$ is:

$$\eta = \frac{V_{\text{MnOOH}}}{V_{\text{oxide}}} = \frac{(M_{\text{MnOOH}}*n_{\text{MnOOH}}/\rho_{\text{MnOOH}})}{(M_{\text{oxide}}*n_{\text{oxide}}/\rho_{\text{oxide}})}$$  
(S2)

It can be noticed that the specific weight is either measured or calculated according to:

$$\rho_i = \frac{(M_i * Z)}{(V_{i,\text{cell}} * A)}$$  
(S3)

Where $Z$ is the formula unit per cell, $V_{cell}$ is the volume of the unit cell and $A$ the Avogadro number ($A = 6.023 \times 10^{23}$).

The calculated densities of MnOOH and of the oxides are given in Tab A.2. A description of a natural a manganite ($\gamma$-MnOOH) from the Kalahari manganese field (South Africa) is given by Kohler et al. [60]. The crystal structure of that manganite was space group $P2_1/c$, $a = 5.304(1)$, $b = 5.277(1)$, $c = 5.304(1)$, $\beta = 114.38(2)^\circ$, and $Z = 4$). A clear deviation from the values (a, b, c and $\beta$) tabulated by Roberts et al. [74] (Tab. A.2) gives nevertheless similar result for the density.

Table A.3 suggests that depending from the starting manganese oxide, there will be either a volumetric contraction or expansion ($\eta$-values). These results show that the initial material
should be well-characterized because the clogging of the filter will depend on the nature of
the used oxide. For this reason, the characteristics of a natural MnO$_2$ mineral given by Li et al.
[57] have been used in this work (Tab. A.4). The next section estimates the $\eta$-value for this
natural mineral. Accordingly, each natural or synthetic mineral have to be properly
characterized before used as an additive in Fe$^0$ beds.
Table A.1: Crystallographic characteristics (formula, crystal system, space group) and expression of the volume of the unit cell for manganese oxide minerals.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Group</th>
<th>Formula</th>
<th>System</th>
<th>( V_{\text{unit cell}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganite</td>
<td>B2_1/d</td>
<td>MnOOH</td>
<td>Monoclinic</td>
<td>abc sin(( \beta ))</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>P4_2/mmm</td>
<td>MnO_2</td>
<td>Tetragonal</td>
<td>( a^2c )</td>
</tr>
<tr>
<td>Todorokite</td>
<td>P2/m</td>
<td>(Mn, Ca, Mg)Mn^{IV}O_7\cdot H_2O</td>
<td>Monoclinic</td>
<td>abc sin(( \beta ))</td>
</tr>
<tr>
<td>Birnessite</td>
<td>-</td>
<td>MnO_2</td>
<td>Orthorhombic</td>
<td>abc</td>
</tr>
<tr>
<td>Hausmannite</td>
<td>I4_1/amd</td>
<td>Mn^{II}Mn^{III}O_4</td>
<td>Tetragonal</td>
<td>( a^2c )</td>
</tr>
<tr>
<td>Manganosite</td>
<td>Fm3m</td>
<td>MnO</td>
<td>Cubic</td>
<td>( a^3 )</td>
</tr>
<tr>
<td>Psilomelane</td>
<td>C2/m</td>
<td>BaMn^{II}Mn^{IV}<em>{8}O</em>{16}(OH)_4</td>
<td>Monoclinic</td>
<td>abc sin(( \beta ))</td>
</tr>
</tbody>
</table>
Table A.2: Characteristics of selected manganese oxides. Apart from manganite* \((Z = 4)\), all values are from Roberts et al. [74]. Data for manganite* are from Kohler et al. [60].

<table>
<thead>
<tr>
<th>Mineral</th>
<th>(Z)</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>angle</th>
<th>density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(-)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(\beta) (°)</td>
<td>calc.</td>
</tr>
<tr>
<td>Manganite</td>
<td>8</td>
<td>8.94</td>
<td>5.28</td>
<td>5.74</td>
<td>90</td>
<td>4.30</td>
</tr>
<tr>
<td>Manganite*</td>
<td>4</td>
<td>5.304</td>
<td>5.277</td>
<td>5.304</td>
<td>114.38</td>
<td>4.31</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>2</td>
<td>4.42</td>
<td>4.42</td>
<td>2.87</td>
<td>-</td>
<td>5.148</td>
</tr>
<tr>
<td>Todorokite</td>
<td>3</td>
<td>9.75</td>
<td>2.84</td>
<td>9.59</td>
<td>90</td>
<td>3.49</td>
</tr>
<tr>
<td>Birnessite</td>
<td>3</td>
<td>8.54</td>
<td>15.39</td>
<td>14.29</td>
<td>-</td>
<td>3.0</td>
</tr>
<tr>
<td>Hausmannite</td>
<td>4</td>
<td>5.7621</td>
<td>5.7621</td>
<td>9.4696</td>
<td>-</td>
<td>4.84</td>
</tr>
<tr>
<td>Manganosite</td>
<td>4</td>
<td>4.436</td>
<td>4.436</td>
<td>4.436</td>
<td>-</td>
<td>5.364</td>
</tr>
<tr>
<td>Psilomelane</td>
<td>2</td>
<td>13.929</td>
<td>2.8459</td>
<td>9.678</td>
<td>92,39</td>
<td>6.45</td>
</tr>
</tbody>
</table>
Table A.3: Name, Formula, calculated density, molecular weight and $\eta$-values for the manganese oxide minerals in Tab. A.2. $\eta$ is ratio of the volume of MnOOH to the volume of each oxide (here $n_{\text{MnOOH}} = n_{\text{oxide}}$). If $\eta > 1$, there is an expansion; this is theoretically the case when pyrolusite is used. For birnessite, a compaction is predicted ($\eta < 1$). The $\eta$ values will be slightly different with the measured density but the trends will be similar.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Calculated density</th>
<th>Molecular weight</th>
<th>$\eta$: specific volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>manganite</td>
<td>MnOOH</td>
<td>4310</td>
<td>0.08784</td>
<td>1</td>
</tr>
<tr>
<td>Birnessite</td>
<td>MnO₂</td>
<td>3000</td>
<td>0.08694</td>
<td>0.70</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>MnO₂</td>
<td>5148</td>
<td>0.08694</td>
<td>1.21</td>
</tr>
</tbody>
</table>
Table A.4: Selected properties of the natural manganese oxide used by Li et al. [57]. The characteristics of pellets are used in this work.

<table>
<thead>
<tr>
<th>Form</th>
<th>Mn (%)</th>
<th>Sp. gravity</th>
<th>Bulk density</th>
<th>Porosity (%)</th>
<th>SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet</td>
<td>53.5</td>
<td>3.58</td>
<td>1.35</td>
<td>0.62</td>
<td>14.9</td>
</tr>
<tr>
<td>Powder</td>
<td>53.5</td>
<td>3.58</td>
<td>2.05</td>
<td>0.43</td>
<td>12.2</td>
</tr>
</tbody>
</table>
A.2: Estimation of the volumetric expansion coefficient for natural MnO\textsubscript{2} mineral

A natural porous MnO\textsubscript{2} mineral with the bulk density $\rho_{\text{min}}$, a porosity $\phi_{\text{min}}$, and a MnO\textsubscript{2} content $x_{\text{MnO}_2}$ is used. A mass ($M_{\text{min}}$) of this sample occupies a volume $V_{\text{min}}$ given by:

$$V_{\text{min}} = V_{\text{MnO}_2} + V_{\text{gangue}} + V_{\text{void}} \quad (S4)$$

Where $V_{\text{gangue}}$ is the volume of the supposedly inert material (called gangue) that is disseminated in MnO\textsubscript{2} and represents a fraction of $(1 - x_{\text{MnO}_2})$ of the mass of solid material.

 Accordingly, the mass of the mineral is given by:

$$M_{\text{min}} = M_{\text{MnO}_2} + M_{\text{gangue}} \quad (S5)$$

Per definition, $V_{\text{void}} = \phi_{\text{min}} \times V_{\text{min}}$ and $S4$ is read:

$$V_{\text{MnO}_2} + V_{\text{gangue}} = V_{\text{min}} (1 - \phi_{\text{min}}) = (M_{\text{min}}/\rho_{\text{min}})*(1 - \phi_{\text{min}}) \quad (S6)$$

The task is to give an expression of $V_{\text{MnO}_2}$ as function of all known parameters. The relation between the mass of MnO\textsubscript{2} in the mineral ($M_{\text{MnO}_2}$), the mass of the gangue ($M_{\text{gangue}}$) and the mass of the mineral ($M_{\text{min}}$) is given by:

$$M_{\text{MnO}_2} = x_{\text{MnO}_2} \times M_{\text{min}}, \quad (x_{\text{MnO}_2} < 1) \quad (S7a)$$

$$M_{\text{gangue}} = (1 - x_{\text{MnO}_2}) \times M_{\text{min}} \quad (S7b)$$

Per definition, $M_{\text{min}} = \rho_{\text{min}} \times V_{\text{min}}$. This expression gives $V_{\text{min}}$ which can be used in Eq. $S6$ to have $(V_{\text{MnO}_2} + V_{\text{gangue}})$. Knowing the real volume occupied by MnO\textsubscript{2} and the gangue in the mineral, the open issue is to calculate the volume of MnOOH resulting from MnO\textsubscript{2}.

The volume occupied by MnOOH is given by:

$$V_{\text{MnOOH}} = M_{\text{MnOOH}}/\rho_{\text{MnOOH}} = M_{\text{MnOOH}} \times n_{\text{MnOOH}}/\rho_{\text{MnOOH}} \quad (S8a)$$

$$V_{\text{MnOOH}} = M_{\text{MnOOH}} \times n_{\text{MnOOH}}/(M_{\text{MnOOH}} \times Z) \times (V_{\text{cell}} \times A) = (A/Z) \times n_{\text{MnOOH}} \times V_{\text{cell}} \quad (S8b)$$

Where $A$ is the Avogadro constant $(6.023 \times 10^{23})$, $n_{\text{MnOOH}} = M_{\text{MnOOH}}/87.84$; $M_{\text{MnOOH}} = 87.84$ g/mol the molar weight of MnOOH, and $V_{\text{cell}}$ the volume of the unit cell of MnOOH. It can be noticed that $n_{\text{MnOOH}} = n_{\text{MnO}_2} = M_{\text{MnO}_2}/86.94$; $M_{\text{MnO}_2} = 86.94$ g/mol the molar weight of MnO\textsubscript{2}.  

35
The coefficient of volumetric compaction or expansion (η) is then given by the ratio 
\[ \eta = \frac{V_{\text{MnOOH}}}{V_{\text{MnO}_2}}. \]
But one needs an approximation to evaluate \( V_{\text{MnO}_2} \) in Eq. S3. One plausible
approximation is to consider the gangue as quartz and deduce the volume \( V_{\text{gangue}} \) from the
relation \( M_{\text{gangue}} = \rho_{\text{quartz}} \cdot V_{\text{gangue}} \). \( M_{\text{gangue}} \) is given by Eq. S4a.

\[ V_{\text{gangue}} = \frac{M_{\text{gangue}}}{\rho_{\text{quartz}}} = \frac{(1 - x_{\text{MnO}_2}) \cdot M_{\text{min}}}{\rho_{\text{quartz}}} \] \hspace{1cm} (S9)

So that the volume \( V_{\text{MnO}_2} \) is given by:

\[ V_{\text{MnO}_2} = \frac{(M_{\text{min}}/\rho_{\text{min}}) \cdot (1 - \phi_{\text{min}}) - (1 - x_{\text{MnO}_2}) \cdot M_{\text{min}}}{\rho_{\text{quartz}}} \] \hspace{1cm} (S10)

**Illustration**

The volumetric expansion coefficient used for Fig. 2 is calculated using 100 g of mineral
having the characteristics of the pellets from Li et al. [57] (Tab. SI.3). The following values
are given: \( \rho_{\text{min}} = 1.35 \text{ g/cm}^3; \phi_{\text{min}} = 0.62; x_{\text{MnO}_2} = 0.778; M_{\text{min}} = 100 \text{ g}; M_{\text{gangue}} = 22.8 \text{ g}; \)
\( M_{\text{MnO}_2} = 77.8 \text{ g}; \rho_{\text{quartz}} = 2.65 \text{ g/cm}^3. \) Unit cell parameters for MnOOH: structure =
monoclinic, \( a = 8.94, b = 5.28, c = 5.74 \) and \( \beta = 90^\circ. \)

\[ V_{\text{cell}} = a \cdot b \cdot c \cdot \sin \beta, \] \( Z=4. \)

\( 77.8 \text{ g MnO}_2 \) corresponds to 0.895 mole of MnO_2. The quantitative reduction will yield
\( n_{\text{MnOOH}} = 0.895 \) mole.

After S3, \( V_{\text{MnO}_2} + V_{\text{gangue}} = M_{\text{min}}/\rho_{\text{min}} \cdot (1 - \phi_{\text{min}}) = (100/1.35) \cdot (1-0.62) = 28.15 \text{ cm}^3 \)

After S9, \( V_{\text{gangue}} = (1 - 0.778) \cdot 100/2.65 = 8.38 \text{ cm}^3 \)

Accordingly, \( V_{\text{MnO}_2} = 28.15 - 8.38 = 19.77 \text{ cm}^3 \) \((V_{\text{MnO}_2} = 19.77 \text{ cm}^3)\)

After S8b, \( V_{\text{MnOOH}} = (A/4) \cdot (M_{\text{MnO}_2}/86.94) \cdot V_{\text{cell}} \)

\[ = (6.023 \times 10^{23}/4) \cdot 0.895 \cdot 1.35 \times 10^{-22} = 18.59 \text{ cm}^3 \] \((V_{\text{MnOOH}} = 18.59 \text{ cm}^3)\)

The contraction coefficient \( \eta \) is then: \( 18.59/19.77 = 0.94; \eta = 0.94. \)

This result means that when the 77.8 g of MnO_2 in the original mineral in consumed, the
produced MnOOH occupies a volume of 0.94 * 19.77 = 18.59 cm^3. It can be noticed that the
density of the mineral MnO_2 is: \( \rho_{\text{MnO}_2} = 77.8/19.77 = 3.93 \) and is closed to the density of
MnOOH (\( \rho_{\text{MnOOH}} = 4.31. \))