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Characterizing the Reactivity of Metallic Iron for Water Treatment: H₂ Evolution in H₂SO₄ and Uranium Removal Efficiency

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Abstract: Metallic iron (Fe⁰) has been demonstrated as an excellent material for decentralized safe drinking water provision, wastewater treatment and environmental remediation. An open issue for all these applications is the rational material selection or quality assurance. Several methods for assessing Fe⁰ quality have been presented, but all of them are limited to characterizing its initial reactivity. The present study investigates H₂ evolution in an acidic solution (pH 2.0) as an alternative method, while comparing achieved results to those of uranium removal in quiescent batch experiments at neutral pH values. The unique feature of the H₂ evolution experiment is that quantitative H₂ production ceased when the pH reached a value of 3.1. A total of twelve Fe⁰ specimens were tested. The volume of molecular H₂ produced by 2.0 g of each Fe⁰ specimen in 560 mL H₂SO₄ (0.01 M) was monitored for 24 h. Additionally, the extent of U(VI) (0.084 mM) removal from an aqueous solution (20.0 mL) by 0.1 g of Fe⁰ was characterized. All U removal experiments were performed at room temperature (22 ± 2 °C) for 14 days. Results demonstrated the difficulty of comparing Fe⁰ specimens from different sources and confirmed that the elemental composition of Fe⁰ is not a stand-alone determining factor for reactivity. The time-dependent changes of H₂ evolution in H₂SO₄ confirmed that tests in the neutral pH range just address the initial reactivity of Fe⁰ materials. In particular, materials initially reacting very fast would experience a decrease in reactivity in the long-term, and this aspect must be incorporated in designing novel materials and sustainable remediation systems. An idea is proposed that could enable the manufacturing of intrinsically long-term efficient Fe⁰ materials for targeted operations as a function of the geochemistry.

Keywords: hydrogen production; intrinsic reactivity; material selection; uranium removal; zero-valent iron

1. Introduction

Metallic iron (Fe⁰) is a reactive material that has been used to produce solid iron corrosion products (FeCPs), which are excellent contaminant scavengers [1–5]. Fe⁰ has been industrially used for water treatment since the 1850s [1,6–11]. Fe⁰ is a low-cost and readily available material, with demonstrated suitability for the design of decentralized treatment systems for safe drinking water [12] and domestic

wastewater [13]. Therefore, “remediation using Fe⁰” is currently regarded as one of the best available technologies in the global effort to achieve Goal 6 of the UN Sustainable Development Goals (SDGs): Ensure availability and sustainable management of water and sanitation for all [14–16]. However, the Fe⁰ remediation technology as a whole suffers from lack of reliable methods to characterize the intrinsic reactivity of used materials [17–23].

Information regarding the intrinsic reactivity of Fe⁰ materials for water treatment is confusing. Li et al. [21] recently summarized the state-of-the-art knowledge on the characterization methods of Fe⁰ for water treatment. This excellent review article with 247 references concluded that due to the inherent limitations of each technique, no single characterization method on its own can “offer all of the necessary information” for the rational selection of Fe⁰ materials for field applications. However, the approaches used by the large majority of articles reviewed by Li et al. [21] were limited to characterizing the pristine Fe⁰ specimens before and after equilibration with contaminants. In a few cases, the systems were characterized at start, at selected time intervals, and at the end of the experiments [24–26]. As a way forward, Li et al. [21] suggested the need to systematically characterize Fe⁰/H₂O systems several times during the experiment and use the results to interpret their contaminant removal efficiency in a holistic approach. However, this approach is time-consuming, expensive, and not even accessible to lowly equipped laboratories such as those in the developing world [27,28]. In other words, the rational approach suggested by Li et al. [21] will be of little help if research institutions with limited instrumental facilities are to contribute to “effectively translate existing knowledge into practical solutions” [14,29]. Therefore, efficient and affordable approaches that can be applied in lowly equipped laboratories are urgently needed to characterize the intrinsic reactivity of Fe⁰ materials. In fact, the chemistry of the Fe⁰/H₂O system could support this effort.

Table 1 summarizes some relevant reactions that can be used as a basis for the development of approaches for the evaluation of the efficiency of Fe⁰/H₂O systems for water treatment. Equation (1) corresponds to the electrochemical dissolution of Fe⁰ by water (iron corrosion) and shows that Fe⁰ can be universally used to produce H₂ [30]. In other words, the stoichiometry of Equation (1) can be used to achieve the following: (i) characterize the extent of iron corrosion [31,32] and (ii) determine the iron content of Fe⁰-based materials [19,33]. The reaction shown in Equation (1) is more intensive at acidic pH values (consumption of H⁺) than under alkaline conditions. In fact, at pH ≤ 4.5, iron corrosion occurs according to the “H₂ evolution” mechanism (Table 2). For higher pH values, iron corrodes according to the “O₂ adsorption” mechanism (Table 2). The expression “O₂ adsorption” corresponds to the old view that iron is corroded by molecular O₂ [34]. It is well-established that at pH > 4.5, a heterogeneous oxide scale develops on the Fe⁰ surface as shown in Equations (2) to (4), and this scale is responsible for contaminant removal in Fe⁰/H₂O systems [8,10,16,28,35,36]. The strong interactions of the oxide scale with several contaminants (including U(VI)) have been identified as a key confounding factor in efforts to characterize the reactivity of Fe⁰ materials for water treatment [24,37]. This situation has motivated Noubactep et al. [38] to introduce ligand-based tools for reactivity characterization (e.g., EDTA test). Our research group used Ethylenediaminetetraacetic acid (EDTA) to complex Fe^{II} and delay formation of solid FeCPS. Recently, Lufingo et al. [22] successfully tested 1,10-Phenanthroline (Phen) as a better complexing agent for characterizing Fe⁰ specimens (Phen test). For each test, the slope of the line [Fe] = f(t) (k_{EDTA} and k_{Phen}) represents the initial corrosion rate.

Table 1. Some relevant reactions for the discussion of the efficiency of metallic iron (Fe^0) in remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems.

Process	Reaction		
Iron oxidation	$\text{Fe}^0 + 2 \text{H}^+$	$\rightleftharpoons$	$\text{Fe}^{2+} + \text{H}_2$
Formation of $\text{Fe}(\text{OH})_2$	$\text{Fe}^{2+} + 2 \text{OH}^-$	$\rightleftharpoons$	$\text{Fe}(\text{OH})_2$
Formation of $\text{Fe}(\text{OH})_3$	$2 \text{Fe}(\text{OH})_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O}$	$\rightleftharpoons$	$2 \text{Fe}(\text{OH})_3$
Aging of $\text{Fe}(\text{OH})_3$	$\text{Fe}(\text{OH})_3$	$\rightleftharpoons$	$\text{FeOOH}; \text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4$
Fe^{2+} complexation	$\text{Fe}^{2+} + \text{EDTA}$	$\rightleftharpoons$	$\text{Fe}(\text{EDTA})^{2-}$

Table 2 summarizes the state-of-the-art knowledge on using the stoichiometry of Equation (1) to characterize the intrinsic reactivity of Fe^0 materials. All other available tools are based on the stoichiometry of secondary reactions as it is now established that contaminant reduction by Fe^0 (electrons from Fe^0) is impossible under environmental conditions [10,36,39,40]. Further, adsorption and co-precipitation with in situ generated FeCPs are the fundamental mechanisms of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems [8,10,16,36,37]. In this work, uranium removal in different $\text{Fe}^0/\text{H}_2\text{O}$ systems is used as representative of contaminant removal-based tools to discuss the suitability of H_2 evolution as an alternative tool to assist material selection for field application.

Table 2. Comparison of used Fe^0 reactivity characterization methods for materials selection for water treatment.

Method	Fe^0 Dissolution in H_2SO_4	Fe^0 Dissolution in H_2O	Fe^0 Dissolution in Complexing Solutions (EDTA, Phen)
Test conditions	$2.0 \leq \text{pH} \leq 3.1$	Neutral pH	Neutral pH
Monitored parameter	H_2 volume	H_2 volume	Fe concentration
Test duration (hours)	24	$200 \leq t \leq 3840$	$24 \leq t \leq 96$
Used Fe^0 mass (g)	2.0	$75 \leq m \leq 600$	$0.01 \leq m \leq 0.10$
Number of used chemicals	1	0	1 to 4
Corrosion mechanism	H_2 evolution	O_2 adsorption	O_2 adsorption
Advantages	Uses only lab accessories and H_2SO_4 , no scientific instrument;	Uses no scientific instrument. Fe^0 corrosion is not artificially accelerated.	Controls Fe^0 corrosion to make it a linear function of time; Simulates natural conditions; Uses only a spectrophotometer.
	Enables the exhaustion of Fe^0 dissolution within a reasonable time.		
Disadvantages	H_2 evolution is not the mechanism occurring in natural systems and water filters.	Measured H_2 volume represents an excess and cannot be strictly related to the stoichiometry of Equation (1); The experiments last for longer time and needs larger Fe^0 amounts	Only the initial dissolution kinetics are recorded; In the EDTA test, Fe dissolved from corrosion products (hydroxides and oxides) are also recorded.
References	Noubactep [32], This study	Reardon [31,41]	Lufingo et al. [22], Noubactep et al. [38]

Fe^0 materials used for water treatment are not originally manufactured for this purpose [42,43]. Hence, they do not show any compositional characteristics making them particularly suitable for the subsurface applications [17–19,21]. In fact, among the factors influencing the long-term behavior of Fe^0 (e.g., crystallinity, iron impurity, surface state, morphology), only the surface state and the morphology can probably be characterized in short-term laboratory experiments. Therefore, methods to characterize or simulate the long-term reactivity of Fe^0 materials for water treatment are still needed. This understanding is also crucial for the design and manufacture of new Fe^0 materials with tailored contaminant removal efficiency.

The objectives of this study are to (i) test selected Fe^0 for their hydrogen production in an acidic solution, (ii) compare their capacity to remove U(VI) from an aqueous solution, and (iii) discuss the trends in the long-term efficiency of Fe^0 materials for water treatment.

2. Experimental Section

2.1. Iron Materials

A total of twelve iron materials was selected and used in this study. Four of them were commercially available Fe⁰ materials for groundwater remediation termed as: (i) “DRI”, (ii) “GGG”, (iii) “HGG”, and (iv) “HGM”. DRI is Eisenschwamm from ISPAT GmbH, Hamburg; GGG is Graugußeisengranulat from G. Maier Metallpulver GmbH, Rheinfelden; HGG is Hartgußgranulat from Hermens; and HGM is Hartgußstrahlmittel from Würth—all in Germany. DRI is a direct reduced iron, while the other materials were cast irons with different geometrical shapes. The other four materials were model carbon steels termed as: (i) “C15”, (ii) “C45”, (iii) “C60”, and (iv) “C100”, primarily differing in their carbon content (i.e., 0.15%, 0.45%, 0.60%, and 1.00%, respectively). Two other selected iron materials were mild steels of different classes termed as: (i) “ST1” and (ii) “ST2”. ST1 had an elevated chromium content (8.6% Cr), while ST2 had an elevated sulfur content (0.287% S). The remaining two materials were scrap irons from a metal recycling company (Metallaufbereitung Zwickau) termed as: (i) “S15” and (ii) “S69”. S15 was a mixture of mild steels from various origins, while S69 was a similar mixture of cast irons.

Apart from DRI, the commercially available Fe⁰ materials were used in their typical state and form (i.e., “as received” state). All other samples were crushed into small pieces, sieved and the particles sizes ranging between 1.0 and 1.6 mm were used in the experiments without any further pre-treatment.

Table 3 summarizes the elemental compositions of the materials based on analyses made using X-Ray fluorescence spectrometry. Figure 1 presents an overview of the distribution of iron impurities in the selected materials. It can be clearly seen that the materials primarily differ in their carbon (C) and silicon (Si) contents. Thus, based on the C content, the tested materials can be divided into three classes: (i) GGG, HGG, HGM, and S69 containing more than 3% C (cast irons), (ii) the seven other materials containing less than 2% C, and mild steels, and (iii) DRI (1.9% C), belonging to the third class, characterized by a specific manufacturing technology, which yielded porous materials [6,44]. All these materials were irregular in shape (filings and shavings) with rough surfaces. An exception was HGM, which had a regular spherical shape, homogeneous size ($\phi = 1.2$ mm), and a smooth surface. DRI had a very rough surface and even porosity. HGM and the two scrap irons (S15 and S69) were visibly covered with rust, whereas all the other materials retained their metallic glaze.

Table 3. Elemental composition of iron materials used in this study.

Fe ⁰	Element (%)								
	C	Si	Mn	P	S	Cr	Mo	Ni	Fe
ST1	0.49	2.80	0.40	0.011	0.003	8.60	0.03	0.15	87.52
ST2	0.15	0.05	1.34	0.068	0.287	0.12	0.03	0.08	97.88
C15	0.12	0.26	0.62	0.019	0.023	0.084	n.d. *	0.055	bal. **
C45	0.48	0.22	0.70	0.012	0.038	0.12	n.d.	0.13	bal.
C60	0.59	0.29	0.65	0.007	0.027	0.19	n.d.	0.093	bal.
C100	0.99	0.25	0.22	0.002	0.008	0.078	n.d.	0.051	bal.
DRI	1.96	0.12	0.09	0.027	0.14	0.003	n.d.	<0.001	bal.
GGG	3.13	2.17	0.36	0.022	0.029	0.077	n.d.	0.056	bal.
HGG	3.13	0.17	0.42	0.053	0.065	0.16	n.d.	0.23	bal.
HGM	3.39	0.41	1.10	n.d.	0.105	0.34	n.d.	0.088	bal.
S69	3.52	2.12	0.93	n.d.	n.d.	0.66	n.d.	n.d.	bal.
S15	0.45	0.28	0.78	n.d.	n.d.	2.67	n.d.	1.34	bal.

(*) n.d. = not determined and (**) bal. = balance.

Figure 1. Distribution of carbon (C), silicon (Si), phosphorus (P), and sulfur (S) in the used iron materials as a function of their manganese content (% Mn). The represented lines (for P and S) are not fitting functions but just join the points to ease visualization. The codes of the individual materials are indicated on the curve for carbon content based on data from Table 3.

2.2. Experimental Methods

2.2.1. Hydrogen Evolution

A total of 2.0 g of each Fe^0 material was allowed to react in a glass washing bottle (500 mL graduated capacity) for 28 h with 0.01 M H_2SO_4 (pH = 2.0) at a constant temperature of $22 \pm 2^\circ\text{C}$. During the course of the experiment, the volume of molecular hydrogen (H_2) produced was directly measured as a function of time. Measurements were done using the experimental setup described in Figure 2 [32]. The washing bottle was connected to a pneumatic trough using a rubber tube. The produced H_2 was collected in a graduated burette, initially filled with tap water. The produced H_2 could then fill the burette by displacing the water in it. The total volume of the solution in the glass wash bottle was 560 mL and contained 2820 mg/L of SO_4^{2-} and 10.5 mg/L of SiO_2 . The total volume of H_2SO_4 was used to reduce the head space in the reaction vessels (washing bottle). The addition of SiO_2 and SO_4^{2-} and the corresponding concentrations were from a laboratory manual on corrosion testing (Manfred Paul—personal communication). The hydrogen production stopped when the pH value was about 3.0 to 3.2. The iron concentration at the end of the experiment was about 21 mM (1176 mg/L).

Figure 2. Schematic diagram of the pneumatic trough for the collection of H_2 . H_2 generated in the washing glass induces the displacement of water in the inverted burette. The H_2 volume corresponds to that of displaced water.

2.2.2. Uranium Removal

The experiments for uranium removal were performed in triplicates. A total of 0.1 g of each Fe^0 material was allowed to react for 14 days in sealed and graduated assay tubes containing 20.0 mL of a U(VI) solution (20 mg L^{-1} or 0.084 mM) under ambient laboratory temperature ($22 \pm 2 \text{ }^\circ\text{C}$). The U(VI) solution was prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ in tap water. The used assay tubes had a graduated capacity of 16.0 mL, but the total volume was used to reduce the head space in the reaction vessels. The resulting Fe^0 mass loading was 5 g L^{-1} . The experiments were conducted with the tap water of the city of Freiberg (Saxony, Germany), with an average composition (mg L^{-1}) of: Cl^- : 7.5; NO_3^- : 17.5; SO_4^{2-} : 42.0; Na^+ : 7.1; K^+ : 1.6; Mg^{2+} : 6.8; Ca^{2+} : 37.1, and its initial pH was 8.4. The tubes were not agitated but turned up-side down at the beginning of the equilibration and then allowed to react undisturbed (quiescent experiments). The tubes were shielded from direct sunlight and left on the laboratory bench for the duration of the experiment.

2.3. Analytical Methods

Analysis for uranium was performed after reduction to U(IV) with the Asernazo III method ([45] and references cited therein). Uranium concentrations were determined by a HACH UV-Visible Spectrophotometer at a wavelength of 665.0 nm using 1.0 cm glass cells. Dissolved iron was determined using FerroVer iron reagent [46]. All chemicals and reagents used for experiments and analysis were of analytical grade. The pH values were measured by combined glass electrodes (WTW Co., Weinheim, Germany). The electrodes were calibrated with nine standards following a multi-point calibration protocol [47] and in agreement with the new IUPAC recommendation [48].

2.4. Expression of the Experimental Results

In order to characterize the magnitude of the tested materials for uranium removal, the removal efficiency (E) was calculated (Equation (6)):

$$E = [1 - (C/C_0)] \times 100\% \quad (6)$$

where C_0 is the initial solution uranium concentration (20.0 mg L^{-1}), while C gives the residual uranium concentration after the removal experiment.

Correlation was used to determine the relationship between the H_2 produced and uranium removal efficiency (E) and k_{EDTA} using SPSS. The correlation coefficient (r) was used to assess the goodness of fit at probability level $p = 0.05$.

3. Results and Discussion

3.1. Molecular Hydrogen Production

Figure 3a–c summarizes the results of the H_2 production experiments for all tested materials. In each figure, the curve for S69 is included for comparison. It can be seen from these figures that the behaviors of most materials are very similar. A typical H_2 production curve can be divided into three stages: (i) Stage 1 is characterized by a rapid increase of H_2 production rate, (ii) Stage 2 is characterized by a slower H_2 production rate and a relatively short plateau, and (iii) Stage 3 is characterized by the continuous decrease of the H_2 production rate.

Figure 3. Cont.

Figure 3. Rate of molecular hydrogen production (V_{H_2}) as a function of time for the Fe^0 materials tested in this work: (a) ST1, ST2, and S69; (b) model mild steels (C15, C45, C60, C100) and scrap irons (S15, S69); (c) commercial Fe^0 (GGG, HGG, HGM, DRI) and S69. The experiments were conducted at 22 ± 2 °C. ZVI stands for Fe^0 . The represented lines are not fitting functions, but they just connect points to ease visualization.

Apart from ST1 and ST2 experiments, which were terminated after 16 h, the recordings of the volumes of H_2 produced by individual Fe^0 materials were stopped after 24 h. However, to enable a good comparative discussion, Figure 3 presents only the evolutions of the H_2 production rates recorded during the first 16 h of experiment for all materials. Changes in the concentrations of H^+ (pH value) and iron were not recorded. It is however obvious that both values continuously increased until the end of the experiment [32]. Table 4 summarizes these results.

It can be seen from Table 4 and Figure 3 that the H_2 evolution of the individual systems was different. For example, the volume of H_2 produced after 24 h varied from 40 mL for HGM to 149 mL for DRI, while the values for ST1 and ST2 were 152 and 192 mL, respectively, after only 16 h. The time at which the maximum H_2 production rate was achieved varied between 0.1 h for DRI and 5.9 h for HGG. According to Reardon [41], the in-situ formed FeCPs shielding the pristine Fe^0 surface strongly influence the H_2 production rate, and its dissolution increases the pH without producing H_2 . This is a plausible explanation for the relatively lower H_2 production of S15 and S69. However, the very low capacity of HGM at producing H_2 cannot only be justified by the presence of FeCPs. Even its smooth surface and regular spherical form are possibly not the only reasons for this low efficiency. For a better discussion, data on the thermal treatment of materials during their manufacturing process are needed [18,19,21,43]. The temperature to which a material is heated can significantly influence its reactivity [49–51]. For example, Scendo and Szczerba [51] observed that the thermal treatment of C45 mild steel coated with WC-5Co-15Al₂O₃ at 800 °C increases its initial corrosion rate by more than four times compared to a material of the same specimen treated at 400 °C. In the same study, coating was done using Al₂O₃ to increase the material resistance to chemical corrosion as suggested by thermogravimetric measurements. It is therefore likely that thermal treatment could have suppressed the reactivity of HGM. Consequently, the best way to bring clarity to this question is to manufacture and test a set of several forms of iron materials from the same initial bulk material. This will elucidate the effects of material manufacturing process on reactivity.

Table 4. Summary of the results of hydrogen (H_2) production in H_2SO_4 (pH 2) and percentage removal (E) of uranium by Fe^0 materials in tap water. $(V_{H_2})_{24}$ is the H_2 volume after 24 h; v_{max} is the maximum H_2 production rate at time t_{vmax} ; [Fe] is the aqueous iron concentration at the end of the H_2 production experiment (28 h). k_{EDTA} is the corrosion rate in a 2 mM EDTA solution [42].

Fe^0	$(V_{H_2})_{24}$ (mL)	v_{max} (mL/min)	t_{vmax} (h)	[Fe] (mM)	E (%)	k_{EDTA} (M h ⁻¹)
ST1 **	152	0.24	2.7	22.1	76	1.35
ST2 **	192	0.31	3.8	25.2	80	1.95
C15	131	0.20	5.0	n.d. *	84	1.92
C45	122	0.28	1.2	n.d.	82	1.95
C60	104	0.22	5.2	n.d.	86	1.94
C100	109	0.23	2.5	n.d.	87	1.83
DRI	149	1.05	0.1	22.4	91	1.86
GGG	137	0.22	1.7	21.7	88	1.82
HGG	109	0.20	5.9	21.8	78	1.54
HGM	40	0.05	1.4	12.8	82	1.55
S15	108	0.30	3.2	19.8	89	1.98
S69	118	0.24	2.5	22.3	93	2.06

(*) n.d. = not determined; (**) H_2 production; the experiment was stopped after 16 h.

Figure 3c shows the most important aspect of the H_2 production experiment. The curves for DRI, HGG, and HGM are representative for all materials and will be discussed later (Section 4.2). In fact, only DRI and HGM are primarily different from all other materials. The H_2 production rate is very fast for DRI and stops after about 8 h. The H_2 production rate for HGG follows the typical 3-stage curve described above. Specifically, the H_2 production rate for HGM begins very slowly, reaching a maximum after 1.4 h, and then remains constant for the rest of the experiment (i.e., even after 16 h). A discussion on the significance of these different profiles for the long-term performance of Fe^0 materials will be given later (Section 4.2).

3.2. Uranium Removal

Table 4 summarizes the results of uranium removal by the Fe^0 materials in tap water. It can be seen from Table 4 that under the given experimental conditions the per cent total removal of uranium (E) varies from 76% for ST1 to 93% for S69. The order of uranium removal efficiencies increased as follows: ST1 < HGG < ST2 < HGM < C45 < C15 < C60 < C100 < GGG < S15 < DRI < S69. From this trend, it is obvious that uranium removal is influenced by many factors. First, a comparison of HGM and HGG (cast irons) shows that HGM with a smooth surface depicted a greater removal efficiency than that of HGG. A similar observation is made when comparing the efficiencies of rough S69 to that of rough and porous DRI. Second, HGM covered with rust was slightly more efficient (82%) at removing uranium from the aqueous solution than ST2 with metal glaze appearance (80%). This result seems obvious but is pointed out because the difference was not really significant (2%). Finally, S15 and C100 (mild steels) were more efficient at uranium removal than HGM and HGG (cast irons). Under such experimental conditions, uranium is removed from the aqueous phase via co-precipitation with aging FeCPs [38,52,53]. In the absence of any pre-treatments, for materials initially covered with rust, adsorption onto rust will surely occur first. This explains why, compared to the other Fe^0 materials, the initially rusted Fe^0 materials (i.e., S69, S15, and rough and porous DRI) depicted the greatest removal efficiencies (E values). This experiment has shown that the surface state (roughness), the porosity (surface area), and the oxidation state (rust presence) of Fe^0 materials can affect their reactivity under near-natural conditions.

3.3. Comparing H_2 Production and Uranium Removal

Figure 4 compares the volume of produced molecular hydrogen (H_2) and uranium removal efficiency as a function of the manganese content (% Mn) of the tested materials. The volume of H_2 produced by individual materials varies from 40 mL for HGM to 192 mL for ST2. The increasing order of the material performances at producing H_2 as confirmed by Table 4 is as follows: HGM < C60 < S15 < HGG $\approx$ C100 < S69 < C45 < C15 < GGG < DRI < ST1 < ST2. Notably, the increasing order for total uranium removal efficiency (E values) by the various materials is not different from the trend presented in Section 3.2: ST1 < HGG < ST2 < HGM < C45 < C15 < C60 < C100 < GGG < S15 < DRI < S69. A comparative analysis from Figure 4 clearly shows that data are scattered, without any trend. This suggests that H_2 evolution and uranium removal are two independent processes. In fact, it can be clearly seen that the highest values of one do not always directly correspond, on average, to the highest nor the lowest values of the other. The following results clearly illustrate the lack of a trend: (i) the material which produced the highest volume of H_2 (ST2) was among the least efficient materials at removing uranium; (ii) DRI was on one hand among the materials with the highest E values, and on the other hand, equally among those which produced the highest H_2 volume; (iii) HGM produced the lowest volume of H_2 but performed better at uranium removal than ST2; and (iv) S69 which depicted the greatest uranium removal efficiency was neither among the materials which produced the highest nor the lowest H_2 volume. It thus appears that there is no direct causality relationship between H_2 evolution and uranium removal and vice versa. In other words, unlike with the EDTA test [38], there is no correlation between the H_2 production test and uranium removal. With the EDTA test of Noubactep et al. [38], the dissolution behavior of Fe^0 in a 2.0 mM EDTA complexing solution was found to directly represent the reactivity of Fe^0 materials for uranium removal. Correlation analysis confirmed no significant relationship between H_2 produced and E ($r = -0.168$, $p = 0.3$). However, a weak but significant relationship was observed between uranium removal efficiency (E) and K_{EDTA} ($r = 0.56$, $p = 0.03$).

Figure 4. Changes of the volume of produced molecular hydrogen (H_2) and the percent U(VI) removal as a function of the manganese content (% Mn). The codes of selected Fe^0 specimens are indicated. The represented lines are not fitting functions, but they just connect points to ease visualization.

In an attempt to develop tests for reactivity characterization for Fe^0 materials used for groundwater remediation or water treatment screening, many research groups have used a comparative study based on contaminant removal in aqueous solution to validate their tests [18,19,22,38,54,55]. Table 5

gives some details about some of these researches. Compared to the H_2 production test evaluated in the current study, which was performed at pH 2, a common point to all the other tests is that they were developed at pH > 4.5. Under this near-natural experimental condition, it can be seen that Noubactep et al. [38] used uranium removal to validate their EDTA test. The EDTA test was years later used as reference by Lufingo et al. [22] to validate the Phen test. Kim et al. [18] used the removal of CAHs and PCP by Fe^0 to validate the Iodine method. CAHs were also used a year earlier by Velimirovic et al. [54] to validate the H_2 evolution at neutral pH values. From this presentation, two key points can be derived: (i) uranium is a reliable compound for validating a Fe^0 reactivity characterization test, and (ii) a correlation between the H_2 production test and a probe contaminant removal by Fe^0 is lacking. This indicates that the production of H_2 under acidic conditions is the main reason why an absence of correlation between the H_2 production test and uranium removal is observed in the present study. In fact, H_2 evolution at pH 2 occurs with a completely different mechanism to that of uranium removal by Fe^0 under environmental conditions. Therefore, the main merit of the H_2 production test as presented in this study is to show the trends of Fe^0 reactivity during the initial phase of the experiment under neutral pH values (Figure 5).

Table 5. Summary of the existing Fe^0 materials reactivity characterization methods validated via comparison of results with that of contaminant removal. “CAHs” stand for “chlorinated aliphatic hydrocarbons” and “PCP” for “Pentachlorophenol”.

Characterization Test	Monitored Parameter	Used Chemical	Compounds Used for Validation	Reference
Iodine method	I_3^- reduction rate constant	Iodine	CAHs and PCP	Kim et al. [18]
Ferric method	Fe concentration	Ferric iron	Cu(II) and TCE	Li et al. [19]
H_2 evolution	H_2 volume	None	CAHs	Velimirovic et al. [54]
EDTA test	Fe concentration	EDTA	U(VI)	Noubactep et al. [38]
Phen test	Fe concentration	1,10 Phenanthroline	EDTA test	Lufingo et al. [22]
H_2 evolution	H_2 volume	H_2SO_4	Not validated	This study

Figure 5. Idealized relative reactivity of Fe^0 materials as a function of the reactive barrier service life. The three scenarios are deduced from the reactivity of DRI, HGG, and HGM for H_2 production in H_2SO_4 (pH 2). For illustration purposes, the elapsed time was changed from hours to years, and the normalization of the reactivity was done arbitrarily.

4. Fe⁰ Materials for Water Treatment

4.1. Fe⁰ Materials

Cast iron and mild steel are unequaled in terms of mechanical and physical properties derived from alloying and heat-treatment. Almost all these materials corrode in a wide range of aqueous environments [20,23,33,38,56–58]. Some general statements occur in the literature on the effects of alloying on the corrosion properties of cast iron and mild steel in water [57,59]. Despite the large number of publications about cast iron and mild steel corrosion, the interaction of the alloying components and impurities has not yet been established; rather, only empirical guides exist [21,34,43,60].

In testing Fe⁰ (cast iron and mild steel) for groundwater remediation, controversial results have been reported [21,43,61]. This is not surprising, since the materials were not selected and tested systematically but, rather, in an arbitrary manner. Moreover, it is almost impossible to produce two batches of an iron material with exactly identical properties. Therefore, the effect of alloying element on the efficiency of the material can only be assessed by working with different lots of materials from the same producer and, if possible, manufactured under similar conditions [20,22].

This study confirms the results from previous studies suggesting cast irons as better materials for water treatment than mild steels [61,62]. This choice has been mainly justified by their low cost and ready availability. The mode of their homogeneous surface corrosion induced by the presence of regularly distributed traces of sulfur (S) and carbides (Fe₃C) in their structure are further arguments for their preference [32,60].

Note that cast iron and mild steel such as those currently used for water treatment were originally manufactured and tested for their corrosion resistance. In such manufacturing and testing processes, efforts are made, to exclude corrosive additives or impurities such as sulfur (S) or phosphorus (P) from the resulting materials (Table 3 and Figure 1). Keeping this in mind and considering the demonstrated favorable role of sulfur in the decontamination process with Fe⁰ [37,63,64], it is logical that Fe⁰/S composites have shown increased performance for water treatment [65,66]. Therefore, in manufacturing conventional Fe⁰ materials, efforts have to be undertaken to avoid the presence of classical alloying elements such as Ni and Cr, while additives or impurities that increase contaminant removal can be allowed. This is particularly important, if the materials are to be obtained from recycled materials. If on the contrary, materials are to be obtained from iron ores, there is no need of alloying in the classical sense [6,44]. To sum up, S is to be considered as an alloying element for Fe⁰ materials that are to be manufactured by direct reduction from iron ores [66].

4.2. Long-Term Performance of Fe⁰ Materials

Available or new materials for water treatment have to be tested for their long-term performance as a function of the site-specific conditions. Some insights on the long-term performance of the Fe⁰ material can be gleaned from the three main cases evident in Figure 5. The scenarios have been deduced from Figure 3c by changing the time from hours to years on the x-axes and transforming the H₂ production rate on the y-axes to an arbitrary normalized relative reactivity for DRI, HGG, and HGM. The resulting trends suggest that, in any natural environment, Fe⁰ materials can be sought (newly manufactured or selected from available materials) that are able to react in three different ways. The first class of materials (case 1) encompasses those which react very rapidly in their initial phase of exploitation as a reactive barrier, and the reactivity then decreases continually with the time. This scenario can be helpful for the following conditions: (i) if the contaminant source is well-identified (i.e., point source) and (ii) the contaminant transport to the barrier is rapid, and it is not expected that more contaminant will be produced over time (instantaneous). Typical examples include spillages and once-off leakages from underground utility pipes. In this case, it is possible that the active lifespan of the Fe⁰ material (here 5–8 years) be sufficient for satisfactory decontamination.

The second class of materials (case 2) reacts slowly in the initial phase of the reactive bed operation, and the reactivity increases continually to a maximum (4th to 8th year). Thereafter, the reactivity

decreases progressively with time. Assuming that there is no additional source of contaminant, such a material can assure a satisfactory decontamination for 20 years or more, since its final corrosion rate (i.e., after 16 years) is still considerable (30%). By then, the contaminant concentration should have decreased considerably. Typical real-life examples may include mining sites with potential for generating acid mine drainage, where initial contaminant release may be initially slow, reaching a peak at a given time, before dropping due to exhaustion of the contaminant source.

The third class of materials (case 3) reacts slowly in the initial phase of the reactive bed operation, and the corrosion rate remains constant for decades. It is obvious that this case is the ideal condition being implicitly considered for modelling purposes, even though the “initiation phase” is often ignored. However, little has been done to consider local site-specific aspects such as the nature of pollution source (instantaneous versus continuous) and time evolution of contaminants [32,40].

Taken together, these deductions imply that the suitable materials are not necessarily the most reactive materials as suggested by laboratory experiments based on the current testing approaches [20,22,38,40,67]. In some cases, for a specific application, a mixture of materials from different classes can be helpful. For example, if it is expected that the contaminant concentration will decrease considerably after 3 years and remain constant for a long time, then a mixture of materials from the classes 1 and 2 or classes 1 and 3 can be used. Thus, the suitable material for each remediation problem should be decided on a case-by-case basis taking into account the nature of the pollution sources and its evolution over time.

4.3. Future Perspectives

Fe^0 materials used for water treatment and environmental remediation comprise of iron filings, iron composites (e.g., bimetallics), iron nails, iron wire, nano- Fe^0 including its composites, scrap iron, sponge iron, and steel wool originating from a variety of primary manufacturing processes. Each material is unique in its intrinsic reactivity and so is its efficiency for the treatment of a given polluted water [22,23]. Past efforts to understand the reason for differences in material efficiencies have examined the elemental composition, the metallurgical properties, and the surface properties including the surface area [21,43,68]. The surface of the in situ generated oxide scale has also been examined. The results of three decades of intensive research can be summarized in one statement as follows: There is no apparent correlations arising between observed efficiency for contaminant removal and physico-chemical characteristics of the materials [20–23,42,68].

The large majority of the available works has focused on differentiating the Fe^0 reactivity based on their efficiency for the removal of selected contaminants [19,38]. The shortcomings of this approach have already been largely discussed [18,19,21,22]. It will just be recalled and stressed here that contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems is not an electro-chemical process. Thus, the stoichiometry of iron corrosion cannot be used to assess the extent of Fe^0 depletion. Sixteen (16) years ago, Lee et al. [69] regretted that mechanistic discussions are performed without mass balance considerations, yet this situation has not changed to date [16,28]. The mass balance should start with that of iron. For example, under the experimental conditions of this work, 2.0 g or 35.7 mM of Fe^0 is allowed to dissolve in 0.01 H_2SO_4 . Then, if complete Fe^0 depletion is achieved, 800 cm^3 of molecular H_2 is produced according to Equation (1). Table 4 shows that ST2 is the material releasing the largest H_2 volume (192 cm^3). Thus, the maximum ratio of material depletion was $\frac{1}{4}$ (25%). A similar calculation for the EDTA test reveals that just 0.12% of used material (0.1 g) is depleted at solution saturation. In this case, solution saturation corresponds to $\text{Fe}:\text{EDTA} = 1:1$, equivalent to $[\text{Fe}] = 112 \text{ mg L}^{-1}$ (2 mM). In real systems, Fe^0 dissolution is certainly slower, but the discussion of its impact on the decontamination process is complicated by the evidence that experimental vessels were more or less vigorously mixed, and the mixing intensities were different from one work to another [36,70].

To the best of the authors' knowledge, the H_2 evolution test used herein is novel in the peer-review literature. Only Landis et al. [68] has reported on a similar approach in a conference proceeding. In Landis et al. [68], the authors used a 1:1 HCl digestion of “as received” Fe^0 specimens

(Fe⁰ + atmospheric FeCPs) and monitored the elemental composition of the leachate using inductively coupled plasma (ICP) analyses. On the contrary, the H₂ evolution at pH 2.0 (H₂SO₄-0.01 M) used in the current study is rooted on the evidence that quantitative H₂ production by a fixed amount of Fe⁰ will stop when its dissolution raises the pH to values close to 3.1. Therefore, an artificial system is created, wherein the trends of reactivity of various Fe⁰ specimens can be differentiated. In other words, in the H₂ evolution test under acidic conditions, far more Fe⁰ dissolution occurs than under natural conditions, and Fe⁰ dissolution occurs with a different mechanism. However, a realistic understanding of the trend of the time-dependent Fe⁰ depletion is obtained and should be used as a basis for future modeling works.

For field implementations, fundamental and technical obstacles are expected, which should be addressed for sustainable remediation systems. For example, the formation of FeCPs (Fe hydroxides and oxides) implies a concomitant decrease of the corrosion kinetics, and thus, a decrease of the kinetics of generation of contaminant scavengers with increasing service life. Furthermore, the volumetric expansive nature of aqueous iron corrosion causes a decrease of the hydraulic conductivity in filtration systems [71–73]. In other words, the challenge of the Fe⁰ research community is to design long-term efficient systems, while accounting for two inherent characteristics of aqueous iron corrosion. The two inherent characteristics are: (i) decreased reaction rates due to formation of FeCPs (“reactivity loss”) and (ii) decreased hydraulic conductivity (permeability loss). This statement corresponds to the state-of-the-art knowledge on Fe⁰ filters as summarized thirteen years ago by Henderson and Demond [74]. Yet nearly 22 years later, this has not changed, suggesting that the past two decades can be regarded as lost ones [37]. The root cause for this stagnation was identified by Ghauch [10] and attributed to the refusal of the research community to reconsider the mechanistic discussion. Specifically, the critical reviews of Noubactep [36,70] demonstrating that Fe⁰ is not likely to play any significant direct role (electron transfer) in the documented reductive processes have remained largely ignored. This view is in tune with the concept of Khudenko [75], who used copper salts to induce reductive transformation of organic pollutants by primary iron corrosion products (Fe^{II} and H/H₂ species). In other words, for the rational design of sustainable Fe⁰-based filtration systems, engineers are facing difficulties in determining the appropriate Fe⁰ amount to use and the thickness of the reactive layer [16,76]. The H₂ evolution test presented herein has further deepened the vagueness as it illustrated that an initially very reactive material can become much less reactive after some time. However, revealing this is a chance to systematically conduct long-term pilot testing of Fe⁰-based remediation systems. A rule of thumb is, “no experiment lasting for less than one year can be considered as long enough” as far as long-term testing of filtration systems is concerned [5,23,76].

5. Conclusions

This study supports the evidence that cast irons are more suitable than mild steels for water treatment. Moreover, selected scrap irons can be successfully used instead of commercial materials. Next to the chemical composition of cast iron and middle steels, their surface state (roughness, porosity, corrosion state) appears to determine the efficiency in removing uranium from aqueous solutions. A larger number of parameters seems to influence the contaminant removal. Their individual effects can only be assessed by carefully manufacturing materials and testing them under relevant conditions. It is expected that this approach will enable the manufacture of iron materials appropriate for various site-specific conditions.

Information generated from this study is important for the application of Fe⁰ for remediation processes. While researchers have been concerned about the possible cessation of the remediation process once iron oxides are formed on the surface of metallic iron, Huang et al. [77] for instance showed that, under anoxic conditions, the magnetite coating will not hinder nitrate reduction provided sufficient aqueous Fe²⁺ is present in the system. In fact, iron corrosion (Fe²⁺ production) cannot stop, since the formation of adhesive layer of iron oxides is not possible [16,78–81]. Thus, the most important question now is to know whether in the long-term the produced amount of Fe²⁺ (FeCPs)

will satisfactorily yield the expected remediation effect. Therefore, on the one hand, materials able to corrode intrinsically in the long-term are to be manufactured and tested. On the other hand, the selection of a material for a target application is to be performed in such a way that the corrosion enhancement (or inhibition) in site specific conditions can be taken into account.

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