

Review

Progress in Understanding the Mechanism of Cr^{VI} Removal in Fe⁰-Based Filtration Systems

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Abstract: Hexavalent chromium (Cr^{VI}) compounds are used in a variety of industrial applications and, as a result, large quantities of Cr^{VI} have been released into the environment due to inadequate precautionary measures or accidental releases. Cr^{VI} is highly toxic to most living organisms and a known human carcinogen by inhalation route of exposure. Another major issue of concern about Cr^{VI} compounds is their high mobility, which easily leads to contamination of surface waters, soil, and ground waters. In recent years, attention has been focused on the use of metallic iron (Fe⁰) for the abatement of Cr^{VI} polluted waters. Despite a great deal of research, the mechanisms behind the efficient aqueous Cr^{VI} removal in the presence of Fe⁰ (Fe⁰/H₂O systems) remain deeply controversial. The introduction of the Fe⁰-based filtration technology, at the beginning of 1990s, was coupled with the broad consensus that direct reduction of Cr^{VI} by Fe⁰ was followed by co-precipitation of resulted cations (Cr^{III}, Fe^{III}). This view is still the dominant removal mechanism (reductive-precipitation mechanism) within the Fe⁰ remediation industry. An overview on the literature on the Cr geochemistry suggests that the reductive-precipitation theory should never have been adopted. Moreover, recent investigations recalling that a Fe⁰/H₂O system is an ion-selective one in which electrostatic interactions are of primordial importance is generally overlooked. The present work critically reviews existing knowledge on the Fe⁰/Cr^{VI}/H₂O and Cr^{VI}/H₂O systems, and clearly demonstrates that direct reduction with Fe⁰ followed by precipitation is not acceptable, under environmental relevant conditions, as the sole/main mechanism of Cr^{VI} removal in the presence of Fe⁰.

Keywords: hexavalent chromium; metallic iron; water treatment; removal mechanism; adsorption; reduction; co-precipitation

1. Introduction

Heavy metal pollution has become a major area of concern because of high concentrations released into the environment. Due to their bioaccumulative and non-biodegradable properties, heavy metals can produce cumulative deleterious effects even in low concentrations in a wide variety of aquatic organisms [1]. Chromium may enter the aquatic ecosystems through the discharge of contaminated wastewaters from steelworks, metal finishing chromium electroplating, preservation of wood leather tanning, corrosion control, dyeing of textiles, manufacture of ceramics, catalysts, and pigments, etc. [2–5]. During the last two decades, much research work has been published regarding the use of metallic iron (Fe⁰) for the treatment of hexavalent chromium (Cr^{VI}) contaminated waters. Forms of tested Fe⁰ materials include cast iron, granulated iron, iron chips, iron coils, iron composites, nano-scale iron, powdered iron, sponge iron, and steel wool [6]. None of these material classes is uniform in its reactivity. For example, there are no typical iron fillings with a characteristic range of reactivity. This evidence suggests that the primary reason for controversial reports in the Fe⁰ literature relies on the ill-defined nature of tested and used materials. The present work aims to

critically review information concerning the mechanism of Cr^{VI} removal from contaminated waters in the $\text{Fe}^0/\text{H}_2\text{O}$ system. The popular state-of-the-art knowledge on the mechanism of Cr^{VI} removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems can be read from recent review and overview articles [7–11]. The Cr^{VI} removal path is summarized by Wilkin et al. [9] by the following wording: “Laboratory studies indicate that removal of chromate from aqueous solutions in contact with Fe^0 involves reduction of Cr^{VI} to Cr^{III} coupled to the oxidation of Fe^0 to $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ and subsequent precipitation of insoluble $\text{Fe}^{\text{III}}\text{--Cr}^{\text{III}}(\text{oxy})\text{hydroxides}$ (Pratt et al., 1997; Jeen et al., 2007; Jeen et al., 2008) . . . In field settings, reductive immobilization of chromium likely involves multiple pathways including reaction with dissolved Fe^{II} and reaction with ferrous minerals, including mackinawite.” This statement is representative of the majority of reports on Cr^{VI} removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems. The present work is an attempt to demonstrate the instability of the reductive precipitation concept for Cr^{VI} removal, based on sound facts from the scientific literature. The presentation begins with ancient works dealing with the $\text{Fe}^0/\text{Cr}^{\text{VI}}/\text{H}_2\text{O}$ system that could be regarded as pioneering investigations for the Fe^0 -based filtration technology (Section 2). Section 3 summarizes the most important articles that are regarded as keys for the establishment of the reductive precipitation concept for Cr^{VI} removal in the scientific literature. Section 4 summarizes findings from the environmental geochemistry of chromium that are relevant for the $\text{Fe}^0/\text{H}_2\text{O}$ system. Section 5 gives a critical evaluation demonstrating what went wrong and how it could be better accomplished in the future. Section 6 summarizes the review.

2. Pioneering Investigations on Cr^{VI} Removal in Fe^0 -Based Filters

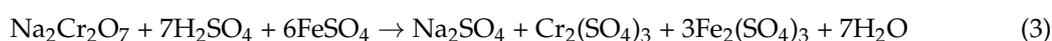
This section presents selected previous work on the $\text{Fe}^0/\text{H}_2\text{O}$ system that should have been properly considered to ease or accelerate research on Cr^{VI} removal in the presence of Fe^0 .

2.1. Hoover and Masseli (1941)

It is now well known that the first process of water treatment based on the use of Fe^0 was described by Henry Medlock in his patent released in 1857. Furthermore, the full-scale water potabilization plant that began service in Antwerp around 1890 was based first on Bischof’s “spongy iron filters”, and then on Anderson’s “revolving purifier” filled with Fe^0 grains [12]; however, the earliest literature reference regarding the Cr^{VI} removal with Fe^0 -based filters, that could be found by the author, was published only in 1941 by Hoover and Masseli [13]. The two authors investigated Cr^{VI} removal from plating wastewater by passing waste chromic acid solutions of varying concentration and acidity through a glass percolator filled with scrap sheet steel punchings. This study also compared the efficiency of Fe^0 with that of several other reducing agents (sodium sulfide, calcium sulfide, barium sulfide, sulfur dioxide, sodium sulfite, sodium bisulfite, calcium bisulfite, zinc hydrosulfite, ferrous sulfate, zinc dust,) used for the removal of aqueous Cr^{VI} . Among all investigated reagents, Fe^0 (iron filings) was considered the most economically feasible [13]. The experimental data revealed that both pH and Cr^{VI} concentration played a key role in the efficiency of wastewater treatment process. The extent of Cr^{VI} removal significantly decreased with increasing pH and Cr^{VI} initial concentration. Another important outcome of this study was the observation that higher Cr^{VI} removal efficiency was obtained when Fe^0 was coated with a layer of copper. Therefore, it can be considered that Hoover and Masseli [13] were also (probably) the first who investigated the use of bimetallic combinations for water treatment, reporting the catalytic effect of a second metal, more noble, coated on Fe^0 , for increased efficiency of water decontamination. Hoover and Masseli also noticed an increase in pH of the column effluent, compared to the influent, and that hydrogen was generated during the process [13]. In spite of all these interesting observations, re-established later by numerous researchers [14], the mechanism of Cr^{VI} removal was not addressed in the work of Hoover and Masseli [13]. However, it can be assumed that they have considered the reduction of Cr^{VI} to Cr^{III} by Fe^0 (direct reduction) as a main mechanism involved in Cr^{VI} removal, as widely used in the cementation process [15,16].

2.2. Case et al. (1969, 1974)

The next important chapter in the history of Cr^{VI} removal with Fe⁰ is the research carried out between 1969 and 1974 by the group headed by O.P. Case (Australia). The starting point of these investigations was the well-documented cementation process, used for the extraction of metals from ores and for the recovery of metals from wastes [16]. In a first study, Case and Jones [17] applied this process to accomplish the simultaneous reduction of Cr^{VI} and precipitation of Cu^{II} present in brass mill effluents. Case and Jones also compared the treatment costs of a medium-sized brass mill effluent contaminated with Cr^{VI} and Cu^{II} via two technologies: (1) by a conventional system utilizing sulfur dioxide, which achieves only Cr^{VI} reduction; and (2) by using scrap iron, for simultaneous removal of Cr^{VI} and Cu^{II}. It was demonstrated that Fe⁰-based treatment was the most advantageous technology, in perfect accordance with previous findings by Hoover and Masseli [13]. Even though this first study of Case and Jones did not investigate the process in a continuous system, it qualitatively demonstrated the feasibility of this treatment process [17]. A subsequent research report [18] continued the research started in 1969 with a more rigorous investigation of the treatment of Cr^{VI} and Cu^{II} polluted wastewaters in Fe⁰/H₂O system. Both batch and dynamic continuous experiments were performed by using soft iron shot (approximately 4.37 mm in diameter) as a reducing agent. The continuous experiments were carried out using a reactor charged with a mixture of scrap iron and glass beads, which had a design very close to that of Anderson's revolving purifier. With regard to Cr^{VI} removal, the author proposed the following mechanism [18]:



At this point, it is important to underline several details: (1) the direct reduction mechanism (Equation (1)) was considered to have the main contribution to Cr^{VI} removal; (2) the iron species resulted from the direct reduction of Cr^{VI} was Fe^{III}; and (3) the source of Fe^{II} acting as reducing agent in the indirect reduction of Cr^{VI} (Equation (3)) was considered to be both Fe⁰ corrosion (Equation (2)) and cementation of Cu^{II} (Equation (4)):



A pH rise was observed during the reduction of Cr^{VI}, in concordance with observations made by Hoover and Masseli [13]; this phenomenon was attributed to the consumption of protons during the process. Under optimal conditions of pH (1.5–3.0), diffusion, and Fe⁰:Cr^{VI} ratio, the reaction was both quantitative and extremely rapid. Cr^{VI} reduction was observed to be more efficient under anoxic conditions. Furthermore, it was noticed that Cu^{II} cementation catalyzes Cr^{VI} reduction [18]. Again, the findings of Hoover and Masseli [13] are corroborated. The work by the group of O.P. Case resulted in the development of a patented rotating reactor for the simultaneous reduction of Cr^{VI} and Cu^{II} cementation from effluents [19].

2.3. McKaveney et al. (1972)

Silicon alloys (mainly of calcium, magnesium, and iron) were used by McKaveney et al. [20], both in batch and column-filtration experiments, for the removal of several heavy metals from water and brine, including Cd^{II}, Cr^{VI}, Cu^{II}, Fe^{II}, Fe^{III}, Hg^{II}, Pb^{II} and Zn^{II}. It was shown by the column experiments that chromium removal only occurred when the alloy had sufficient time to reduce Cr^{VI} to Cr^{III}. However, low Cr^{VI} removal efficiency was reported for the MgFeSi alloy (mass composition: 8.8% Mg, 45.2% Si, 45% Fe) at pH 5.6, compared to removal of all other heavy metals, attributed to a slow kinetics. Therefore, either prolonged contact with the alloy, or acid addition to pH 3.0 was suggested in order to

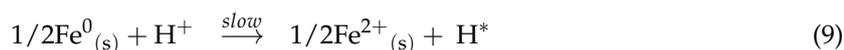
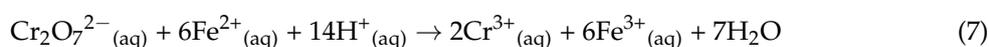
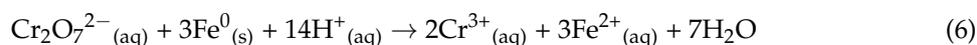
achieve a higher Cr^{VI} removal efficiency. However, such acidic conditions are in contradiction with the working pH recommended to prolong the life of silicon alloys, which should be greater than 4.0. The authors suggested that Si alloys are acting as metallic exchangers and the mechanism responsible for the removal of heavy metals appears to be primarily electrochemical [20], analogous to cementation for divalent ions such as Cu^{II} and Hg^{II} [16]. For elements at higher oxidation states (>2), additional electrochemical mechanisms coupled with hydroxide formation through hydrolysis reactions were also suggested as possible. For instance, it was proposed that a Cr^{VI} removal mechanism should comprise two steps: (1) Cr^{VI} reduction to Cr^{III}, and (2) precipitation of Fe^{III} and Cr^{III} hydroxides [20].

2.4. Gould (1982)

Even though this study was not conducted via column dynamic experiments, it will be, however, discussed here, since, to the best of my knowledge, it can be regarded as the first kinetic study on Cr^{VI} reduction by Fe⁰ [15]. In this work, Gould reported on the effectiveness of relatively pure Fe⁰ in reducing Cr^{VI} to Cr^{III} over a wide range of operational conditions [15]. The overall data presented clearly indicated that reduction rate was dependent on the hydrogen ion concentration (pH), Cr^{VI} concentration, ionic strength, Fe⁰ surface area, and mixing rate. The rate constant increased with increasing Fe⁰ surface area, while decreasing with increasing Cr^{VI} concentration. Increasing ionic strength was found to result in a rapid decrease of the rate constant at ionic strengths below 0.1 M; conversely, at ionic strengths in excess of 0.1 M the rate of reduction appears to be nearly independent of the ionic strength [15]. The rate of reaction increased rapidly as the mixing rate increased from 70 to 300 min⁻¹ (rpm), after which it stabilized sharply. The rate of Cr^{VI} reduction was found to be first order with respect to Fe⁰ surface area and half-order with respect to both Cr^{VI} and H⁺, as results from the following kinetic expression [15]:

$$\frac{dC_{Cr^{VI}}}{dt} = -k[Cr^{VI}]^{0.5}[H^+]^{0.5}A \quad (5)$$

where: k (L cm⁻² min⁻¹) is the rate constant, A is the surface area of iron (cm² L⁻¹), $[Cr^{VI}]$ and $[H^+]$ are the concentrations of Cr^{VI} and H⁺ (mol L⁻¹). Reaction stoichiometry was found to be independent of experimental conditions, with one exception: the initial Cr^{VI} concentration. With regard to the mechanism, this study undoubtedly indicated that Fe⁰ should be regarded not only as a reducing reagent, but also as a generator of secondary reducing reagents (Fe^{II} and H/H₂) [15]. It was suggested that reaction between Cr^{VI} and Fe⁰ involves not only heterogeneous (direct) reduction with Fe⁰ (Equation (6)), but also homogeneous reduction with the secondary reducing reagent Fe^{II} (Equation (7)) produced by the process of Fe⁰ oxidative dissolution (Equations (6) and (8)) [15]:



This is consistent with the mechanism previously proposed by Case [18]. Moreover, based on the observed high efficiency of Cr^{VI} reduction, and because reaction stoichiometry was found to be independent of pH, it was suggested that some other mechanism may also be involved in Cr^{VI} reduction. Both molecular hydrogen (H₂) and some active hydrogen species generated during iron corrosion (Equations (8)–(10)) were considered to act as reductant for Cr^{VI} [15].

2.5. Bowers et al. (1986)

Bowers and co-workers tested the suitability of scrap iron fillings for Cr^{VI} removal from plating wastewaters, using both batch and continuous-flow completely mixed reactors [21]. Results of the kinetic studies carried out over the pH range of 2.0–3.0 indicated that the reaction appears to be zero order with respect to Cr^{VI}, which could suggest that surface oxidation of Fe⁰ to Fe^{II} is the limiting reaction step [21]. In addition, it was noticed that reduction rates of Cr^{VI} strongly increased as pH decreased, in agreement with previous reports [13,15,18]. The mechanism proposed for Cr^{VI} removal comprised two steps: (1) heterogeneous reduction with Fe⁰, and (2) homogeneous reduction with Fe^{II} produced as a result of Fe⁰ oxidative dissolution (Fe⁰ corrosion). Another important outcome of this study was the evidence that Cr^{VI} removal efficiency exceeded the theoretical solubility of Cr(OH)₃ [21], which can be attributed to Cr^{III} adsorption on Fe^{III} hydroxides. In addition, both the settleability and specific resistance of the resultant Cr(OH)₃ sludge were improved dramatically by co-precipitation with Fe(OH)₃. Therefore, the results of Bowers et al. [21] can be regarded as the first hints for the potential importance of adsorption and co-precipitation in the process of Cr^{VI} removal in Fe⁰/H₂O systems.

2.6. Summary

There are several important conclusions that can be drawn from these early studies. First, the efficiency of Fe⁰ in removing Cr^{VI} from aqueous solutions was reported for the first time not 25 years ago, nor 50 years ago; this finding is nearly 80 years old. Second, the mechanism of Cr^{VI} removal, which will be referred to as “reductive precipitation” in papers published starting with the mid-1990s [22], was also suggested much earlier. Third, even though the involved processes have not been studied in detail, it was clearly indicated that Fe⁰ can act not only as a reducing reagent, but also as a generator of secondary reducing reagents, including Fe^{II} and hydrogen species. Fourth, Fe⁰ inevitably generates iron hydroxides/oxides that are adsorbent and, possibly, enmeshing agents for Cr^{VI}. Fifth, even though dichromate (Cr₂O₇²⁻) was the main Cr^{VI} species, the results are transferable to hydrogen chromate and chromate species (HCrO₄⁻, CrO₄²⁻). Summarizing, the Fe⁰/H₂O system contains three different reducing agents for Cr^{VI} chemical transformation: Fe⁰, Fe^{II}, and H/H₂; as far as Cr₂O₇²⁻ (Cr^{VI} species relevant for mining and wastewaters) is concerned, all three reductants are powerful. In particular, reduction of Cr^{VI} at the surface of Fe⁰ is theoretically possible. It is ignored that the transfer of 6 electrons in a reaction involving Fe⁰ and Cr₂O₇²⁻ is practically impossible under environmental conditions.

3. Permeable Reactive Barriers (PRBs) as Fe⁰-Based Filtration Systems for Cr^{VI} Removal

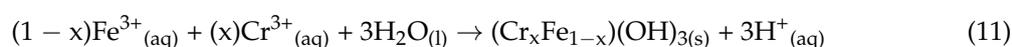
3.1. Background

During the 1980s a new concept emerged in the field of environmental remediation: the idea of using underground permeable reactive barriers (treatment walls) for in situ treatment of polluted groundwater [23,24]. A treatment wall (or a PRB) is a porous reactive or adsorptive medium that is placed in the path of a contaminated groundwater plume with the aim of either to capture the contaminants, or to transform them into less harmful substances, as the groundwater flows through the barrier under the natural hydraulic gradient, or both [25,26]. The main advantages of this concept include: (1) in situ treatment; (2) low operation and maintenance cost; (3) easy of monitoring; (4) no disturbing of the above-ground space due to treatment facilities; (5) treatment of large volumes of water containing low concentration of contaminants; and (6) simultaneous treatment of multiple contaminants [26–29]. Starting with the early 1990s, this concept stimulated considerable research concerning the use of various materials for the treatment of groundwater polluted with a wide range of contaminants. Due to its low cost and high availability, the reactive medium predominately selected for PRBs applications was metallic iron (Fe⁰), largely termed as zerovalent iron (ZVI). ZVI is in essence an ill-defined material encompassing all Fe⁰-based alloys, commercially available as “granular

iron", "iron filings", "iron chips", and "iron shavings", etc. [6,26,28,30,31]. Even though Fe⁰ reactivity toward both inorganic and organic substances was reported much earlier by an important number of works [13,15,17,21,32–34], the use of Fe⁰ as a reactive material for water remediation received a great deal of attention only at the beginning of the 1990s, after the publication of the first experimental studies focused on the degradation of chlorinated aliphatics [35–39].

3.2. Early Laboratory-Scale Investigations for PRBs

There are few laboratory-scale works [22,25,40–42] that have investigated the remediation of Cr^{VI} contaminated waters with Fe⁰ in the first years after Gillham's pioneering studies, and only two of them have actually been carried out by simulation of Fe⁰-based filtration systems (i.e., via column experiments) [25,40]. To the best of my knowledge, the first "post Gillham" work investigating remediation of Cr^{VI} contaminated waters in a Fe⁰-based filtration system was reported by Blowes and Ptacek in 1992 [40]. In this study, three iron-based solids (pyrite, fine-grained (0.5–1 mm) Fe⁰ fillings, and coarse-grained (1–5 mm) Fe⁰ chips) were assessed for their ability to remove aqueous Cr^{VI}, under both batch and dynamic conditions. Column experiments were conducted at flow rates typical of those normally encountered at sites of remediation, using two different reactive mixtures: one containing 50% mass Fe⁰ filings, and the second containing 10% mass Fe⁰ chips; the difference up to 100% was quartz sand (25 < mesh < 30) [40]. Cr^{VI} breakthrough in the column with Fe⁰ chips mixture was observed after treating 4.5 pore volumes, while for the column with Fe⁰ filings mixture Cr^{VI} was absent from effluent for more than 15 pore volumes. In addition, brown coatings, inferred to be ferric oxyhydroxides were observed on the Fe⁰ chips, whereas little formation was noticed on Fe⁰ filings [40]. The reported results suggested that all investigated reactive materials may be used to remove Cr^{VI} at low groundwater velocities; however, aqueous Cr^{VI} removal was most rapid for the fine-grained, and least rapid for coarse-grained Fe⁰; therefore, only fine-grained Fe⁰ was found to be suitable for locations with rapid groundwater flow. Unfortunately, no explanation was given by the authors neither for the observed differences in efficiencies of the two columns, nor for the precipitation of ferric oxyhydroxides with greater intensity on the surface of the Fe⁰ chips [40]. In an extension of the article published in 1992 [40], Blowes and coworkers carried out new column experiments in order to evaluate the ability of four Fe-bearing solids (siderite, pyrite, fine-grained (0.5–1 mm) Fe⁰ fillings, and coarse-grained (1–5 mm) Fe⁰ chips) to remove dissolved Cr^{VI} from synthetic groundwater [25]. While in the 1992 study columns were packed with a reactive mixture comprising one of the three reactive solids, calcite, and quartz [40], in the 1997 study columns were packed with layers of reactive mixtures [25]. The results confirmed that Cr^{VI} removal was most rapid for the Fe⁰ filings, and least rapid for the Fe⁰ chips. Secondary phases such as goethite, lepidocrocite, maghemite, and possibly hematite were identified at the surface of reacted Fe⁰. Even though no discrete chromium mineral was detected, zones within the iron hydroxides contained Cr^{III}; however, while goethite contained up to 27.3% mass Cr(OH)₃, all other phases were low in chromium. Additionally, it was noticed that Cr^{III} was neither associated with all Fe⁰ grains, nor uniformly distributed within specific areas of the iron hydroxides. Since the mass ratio of Fe to Cr was similar to that reported by previous studies (Fe:Cr = 3:1, [43]), it was suggested that Cr^{III} was most probably incorporated into the iron hydroxides; nevertheless, the possibility that Cr^{III} occurred as an adsorbed phase on goethite was not totally discounted [25]. The removal of Cr^{VI} with Fe⁰ was suggested to take place through the same "reductive precipitation" mechanism previously proposed by Cantrell et al. [22]: reduction of Cr^{VI} to Cr^{III} coupled with the oxidation of Fe⁰ to Fe^{II} and Fe^{III}, followed by precipitation of a sparingly soluble Fe^{III}-Cr^{III} (oxy)hydroxide phase [25]:



The long term stability of the Cr-bearing precipitates was also assessed by flushing the column with Cr^{VI}-free calcium carbonate saturated solution; this process was accompanied by a gradual disappearance of the visible ferric oxyhydroxides, attributed to reduction of Fe^{III} by Fe⁰ [25]:



During the leaching test it was observed that chromium concentrations remained below the level of detection (0.05 mg/L) until the experiment was completed, for an additional 350 pore volumes. This was an extremely important result, indicating that Cr^{III} existent in the Fe^{III}-Cr^{III} (oxy)hydroxide phase will remain stable after the input of Cr^{VI} ceases [25].

The mineralogical and geochemical nature of secondary reaction products formed on Fe⁰ fillings and quartz grains throughout the column tests conducted by Blowes et al. [25] were further investigated by Pratt et al. [44]. Coatings on Fe⁰ and quartz grains were identified as goethite; however, while the mineral layer on quartz grains was thin (<25 µm) and compact, Fe⁰ fillings were encrusted with coatings of thickness varying in the 25–50 µm range. The most widespread morphology of goethite was a botryoidal texture, occurring probably at the points of grain contact; nevertheless, euhedral tabular crystals were also observed, occurring most likely in the open interstitial areas between grains [44]. It was also evidenced that all detectable chromium at the Fe⁰ surface existed as Cr^{III} species—the distribution of Cr^{III} was heterogeneous, with the highest concentrations being found at the outermost edges of thin and compact goethite coatings. In addition, iron and chromium ions in the near-surface coatings acquired chemical and structural characteristics similar to Fe₂O₃ and Cr₂O₃, which is distinct from the structure of the bulk phase [44].

3.3. Testing Fe⁰ PRBs for Cr^{VI} Removal at Pilot Scale

The first attempt to transfer the Fe⁰ technology from laboratory bench-scale studies to field implementation was the pilot-scale field PRB initiated in September 1994 at an old hard-chrome plating facility near Elizabeth City, USA. The main objectives of this test were: (1) to evaluate the ability of a Fe⁰-based PRB to remediate, in situ, Cr^{VI} contaminated groundwater; (2) to determine if the results of field tests are consistent with prior laboratory study results; (3) to evaluate the geochemical parameters that may best predict the PRB performance; and (4) to identify mineral phases formed at the surface of PRB that might affect its long-term performance [27]. In addition to chromate (in concentrations up to 12 mg/L), the contaminated groundwater also contained several chlorinated organic compounds, including trichloroethylene, cis-dichloroethylene, and vinyl chloride [45]. The PRB was comprised of four materials, mixed in equal volumes: two types of Fe⁰ (low grade steel waste stock (Ada Iron and Metal, 1–15 mm), and heated cast iron (Master Builder's Supply, 0.2–4 mm)), gravel sand (1–4 mm), and native aquifer solid materials (<0.1 mm). The barrier had a staggered fence design with 21 cylinders (20 cm in diameter) installed from 3 to 8 m below ground surface [27,45]. Monitoring wells located within or down gradient of the iron cylinders revealed chromate concentrations less than 0.01 mg/L, coupled with trichloroethylene removal efficiencies greater than 70%. These "treated zones" were characterized by increased concentrations of dissolved Fe^{II} (2–20 mg/L) and hydrogen (>1000 nM), elevated pH (7.5–9.9), reduced Eh (–100 to +200 mV), low dissolved oxygen (<0.1 mg/L), and the presence of sulfides both in aqueous and solid phases. Instead, in monitoring wells placed in "gaps" where groundwater does not intercept the iron cylinders, the geochemical parameters of groundwater remained essentially unchanged: little change in Cr^{VI} concentration over time, no Fe^{II}, low concentrations of dissolved hydrogen (<10 nM), low pH (5.6–6.1), oxidized Eh (+200 to +400 mV), high dissolved oxygen (0.6–2 mg/L), and absence of sulfides [45]. These geochemical changes were found to be identical to prior laboratory observations [42], being attributed to the following reactions [27]:

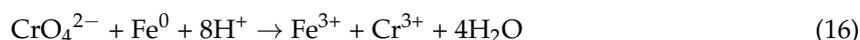


After 20 months of testing, surface analysis of Fe⁰ filings revealed the building of a significant layer of Fe oxide/hydroxide; chromium was also detected, but only at the surface of 1–15 mm Fe⁰. In spite of the observed Fe⁰ passivation, two years after the emplacement of the PRB, there has been no indication of decreased permeability of the reactive mixture [27,45]. This observation disagrees with the concerns raised with regard to system longevity claiming that the maintenance of sufficient permeability within the reactive zone is questionable due to the deposition of secondary mineral layers at the surface of Fe⁰ [46,47]. We can say today, armed with all the knowledge available to us now, that the unaffected porosity may be the result of the PRB design: the PRB was not made from pure Fe⁰, but from a reactive mixture comprising 50% Fe⁰ and 50% inert materials; this is in accord with recent studies that have demonstrated that mixing Fe⁰ and nonexpansive materials prevents the rapid clogging of the Fe⁰-based filters, being thus a pre-requisite for system sustainability [48–50].

3.4. Full Scale Fe⁰ PRBs for Cr^{VI} Removal

3.4.1. Elizabeth CITY (USA)

The success of the pilot-scale test at the Elizabeth City site eventually led to full-scale implementation of the PRB technology, in June 1996. The Fe⁰ PRB had a continuous wall configuration (46 m long, 0.6 m thick, 7.3 m deep) and was designed to remediate overlapping plumes of Cr^{VI} and trichloroethylene [51,52]. Laboratory experiments and cost analysis assessments were carried out prior to installation of the PRB in order to determine the reactive mixture that would be the best suited for simultaneously treating the Cr^{VI} and TCE contaminated groundwater. Based on the results of these studies it was decided that the reactive medium of the PRB will be composed entirely of Peerless granular iron (100% Fe⁰), with an average grain size of 0.4 mm. The total project cost was approximately 985,000 U.S. \$; however, it was anticipated that using this PRB over a 20 year period would result in a saving of 4 million U.S. \$ in operation and maintenance costs, compared to a pump-and-treat system [53]. Monitoring results of this PRB after 15 years of operation indicate consistent removal of Cr^{VI} in any of the down gradient compliance wells, from influent concentrations of up to 10 mg/L to less than 3 µg/L; however, it took almost 2 years for the down gradient concentrations to decrease below remedial goals, due to slow desorption of the contaminants from the aquifer matrix [46,52–56]. The PRB at Elizabeth City was found to be also a long-term sink for C, S, Ca, Si, Mg, N, and Mn present in groundwater [56]. The “reductive precipitation” mechanism was considered to be responsible for the removal of Cr^{VI} at the Elizabeth City PRB [46]. Moreover, it was also assumed that Fe⁰ was oxidized directly to Fe^{III}, as a result of Cr^{VI} reduction to Cr^{III} [46,52–54]:



Ferrous iron detected in treated groundwater was attributed to [52,53,56]: (1) Fe⁰ corrosion (Equation (14)), process that was also responsible for the increased concentration (>1000 nM) of H₂; (2) reductive dissolution of aquifer minerals, due decreased redox potential in regions down gradient from the reactive media; and (3) dissolution of new formed Fe^{II}-bearing mineral phases. Subsequently, the precipitation of highly insoluble mixed Fe^{III}-Cr^{III} hydroxides (Equation (15)) was presumed to take place [51,52].

Primary authigenic precipitates identified in the Elizabeth City PRB were lepidocrocite, magnetite, ferrihydrite, carbonates (aragonite, iron carbonate hydroxide and/or siderite), carbonate green rust, and iron monosulfides (mackinawite) [47,55,56]. Analysis of mineral precipitates evidenced that chromium was present dominantly as Cr^{III} [55]. As expected, the continued buildup of mineral precipitates was found to have a negative impact on the hydraulic performance of PRB. After four years of operation, a 0.032% reduction in porosity was estimated at 2.5 cm into the PRB, while at distances > 8 cm the porosity reduction was <0.002% [56]; instead, after eight years of operation, less than 15% of the total available pore space has been lost [55]. However, rates of mineral accumulation decreased with time, which was believed to indicate a net loss of Fe⁰ “reactivity” [56]. Even though

Fe^{II} concentrations within the PRB increased from background levels (<0.5 mg/L) to as much as 14.8 mg/L, an important number of studies have not taken into consideration neither the coupling of Cr^{VI} reduction with oxidation of Fe^0 to Fe^{II} , nor the reduction of Cr^{VI} with dissolved Fe^{II} [46,52–54]. In this regard, it should be pointed out here that, since the standard potential of the $\text{Fe}^{\text{II}}/\text{Fe}^0$ and $\text{Fe}^{\text{III}}/\text{Fe}^0$ couples is -0.44 and -0.04 V, respectively [57], from thermodynamic perspective it seems that oxidation of Fe^0 to Fe^{II} is considerably more favorable than oxidation of Fe^0 to Fe^{III} ; hence, the oxidation of Fe^0 will probably stop at Fe^{II} , as suggested in previous works [15,18,21]. But, if Fe^{III} was not the result of Cr^{VI} reduction with Fe^0 , then which was the process that generated all the Fe^{III} precipitated in secondary minerals at surface of Fe^0 ? Due to the low concentration of dissolved O_2 (<0.2 mg/L) [52], it is questionable whether oxidation of Fe^{II} by O_2 could be responsible for all the observed Fe^{III} mineral layers. Therefore, it is highly plausible that the presence of Fe^{III} coatings may be explained by an important Cr^{VI} removal pathway, overlooked by many of the aforementioned studies: the indirect reduction of Cr^{VI} with Fe^{II} . This mechanism would be in accord with previous studies reporting that Fe^{II} is a potent reductant of Cr^{VI} . For instance, it was demonstrated that, for equal concentrations of Cr^{VI} and dissolved O_2 , Cr^{VI} oxidizes Fe^{II} faster than O_2 by a factor of 6×10^3 at pH 6, and 1×10^3 at pH 8 [58]. Nevertheless, it should be noted that contribution of indirect reduction with Fe^{II} to the mechanism of Cr^{VI} removal at the Elizabeth City PRB was, however, mentioned in two studies published under the leadership of R.T. Wilkin [55,56]. These works concluded that elevated Fe^{II} concentrations downgradient of the PRB have led to the development of a “reducing zone” where Cr^{VI} is removed from the groundwater. Another important step forward made by the group R.T. Wilkin in elucidating the mechanisms underlying the removal of Cr^{VI} with Fe^0 was the suggestion that some of the Fe^{II} -containing secondary minerals (e.g., mackinawite, carbonate green rust, magnetite) may also support Cr^{VI} removal, either through redox reactions at the mineral-water interface, or by the release of Fe^{II} to solution [55,56].

3.4.2. Willisau (Switzerland)

The Willisau PRB was implemented in November 2003 to treat groundwater contaminated with up to 10 mg/L Cr^{VI} at a former wood impregnation factory that used a chromate solution to preserve timber from deterioration. The PRB had an innovative design, consisting of two different components: (1) a single row of cylinders for lower expected Cr^{VI} concentrations; and (2) an offset double row of cylinders for higher expected Cr^{VI} -concentrations. The reactive filling inside the cylinders ($d = 1.3$ m) was installed from 12 to 23 m below ground surface, and consisted in a mixture of Fe^0 shavings (5–20 mm) and gravel (2–5 mm) in the ratio of 1:3 (by weight); this ratio was selected to ensure an initial permeability of the reactive material approximately three times larger than the surrounding subsoil, and to prevent the rapid clogging of the barrier due to precipitation of secondary phases in pore spaces [59,60]. The double row of cylinders successfully treated the Cr^{VI} contamination at normal groundwater flow velocities (residual Cr^{VI} concentrations < 0.01 mg/L); however, during events of exceptionally high groundwater levels (which result in a substantial mobilization of Cr^{VI}) the remediation effectiveness was only 96%. In contrast to the double row, the remediation capacity of the single row was not efficient enough to reduce the Cr^{VI} concentrations below the critical limit of 0.01 mg/L; this phenomenon was attributed to an inadequate overlap of the cylinders resulting in insufficient concentrations and mixing of dissolved Fe^{II} in the Cr^{VI} -contaminated plume [59]. Surface analysis of Fe^0 and gravel particles sampled after four years of operation showed that, on average, iron occurred in a mixture of goethite ($\sim 60\%$), ferrihydrite ($\sim 30\%$), and a small fraction ($\sim 10\%$) of Fe^{II} , mainly composed of magnetite. In addition, hematite, maghemite and lepidocrocite were also detected. While Cr^{VI} was not detected, Cr^{III} occurred in the form of two different (in terms of Cr/Fe ratio) mixed $\text{Cr}^{\text{III}}\text{-Fe}^{\text{III}}$ hydroxides [60]. Based on these observations, the authors suggested following possible reaction pathways that may contribute to Cr^{VI} removal: (1) heterogeneous reduction of Cr^{VI} with Fe^0 ; (2) heterogeneous reduction of Cr^{VI} with Fe^{II} bearing solids; (3) homogeneous reduction of Cr^{VI} with dissolved Fe^{II} ; and (4) precipitation of the resulted Cr^{III} as mixed $\text{Cr}^{\text{III}}\text{-Fe}^{\text{III}}$ -hydroxides.

However, it was considered that, due to the rapid corrosion of Fe^0 , the direct reduction with Fe^0 was not significant; therefore, only a reduction of Cr^{VI} with Fe^{II} -containing minerals and with dissolved Fe^{II} were taken into consideration as main paths for the first step of Cr^{VI} removal, reduction to Cr^{III} [59,60]. The occurrence of two different Cr^{III} species at the surface of exhausted Fe^0 shavings strongly supports this conclusion: (1) $\text{Cr}^{\text{III}}\text{-Fe}^{\text{III}}$ hydroxides with Cr/Fe ratio $> 1/3$, produced via heterogeneous reduction of Cr^{VI} with Fe^{II} bearing solids; and (2) $\text{Cr}^{\text{III}}\text{-Fe}^{\text{III}}$ hydroxides with Cr/Fe ratio of about $1/3$, resulted from the homogeneous reduction of Cr^{VI} with dissolved Fe^{II} . In addition, the existence of $\text{Cr}^{\text{III}}\text{-Fe}^{\text{III}}$ hydroxides not only on Fe^0 shavings, but also on the surface of gravel particles, further suggested that the homogeneous reduction process with dissolved Fe^{II} , occurring within the pores space, was a very important pathway [60]. Accordingly, one of the main limiting factors for the longevity of the PRB was found to be the availability and accessibility of Fe^{II} [59]. After four years of operation, Fe^0 shavings were found to be covered by a layer of Fe-hydroxides, which lead to a volume increase; nevertheless, the reduction of pore space in the reactive media appeared to be minor [60]. The innovative design of the Willisau PRB possesses several advantages, including: (1) it represents a good geotechnical solution for installation at large depths, in heterogeneous soils; (2) low risk of disturbing the hydrological regime in case the filling material becomes partially clogged by ferric hydroxides; (3) minimizes the amount of reactive material needed, since it partly relies on a dispersive Fe^{II} -plume; and (4) good remediation effectiveness even under exceptionally high groundwater level events [59,60].

3.5. More Recent Laboratory-Scale Reports (Post Elisabeth City PRB)

Following the articles evaluated in the previous sections, more recent studies mainly investigated the practical applicability and long-term efficiency of $\text{Fe}^0/\text{H}_2\text{O}$ systems for Cr^{VI} removal from polluted aqueous solutions. In this context, hundreds of papers were published in the last 20 years, mostly attempting to [14]: (1) study the influence of operational parameters on the efficiency of Cr^{VI} removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems; (2) elucidate the kinetics and mechanism of Cr^{VI} removal; (3) study the nature of secondary mineral phases precipitated at the Fe^0 surface; and (4) find methods to enhance the efficiency of Cr^{VI} removal. With respect to the mechanism of Cr^{VI} removal, the large majority of articles have indicated direct (heterogeneous) reduction with Fe^0 as the main removal pathway [25,27,52,54]. Unfortunately, these reports co-exist in the literature with publications demonstrating that Fe^0 surface is universally covered by oxide layers [61–66], and that Fe^0 is additionally passivated with corrosion products during the remediation process [44,52,61,67,68]. Numerous recent studies, aimed to gain insight into the principles governing the removal of Cr^{VI} in $\text{Fe}^0/\text{H}_2\text{O}$ systems, have also presumed that this process is exclusively the result of direct electron transfer from Fe^0 to Cr^{VI} [69–79]. Since the surface of commercially Fe^0 materials is permanently covered by an outer layer of low electric conductive air-formed oxides (hematite, maghemite) [64], the electron transport from Fe^0 to Cr^{VI} should be severely inhibited [69–79]. Moreover, Fe^0 efficiency should significantly decrease during the time, as its surface is progressively covered with additional secondary mineral coatings that prevents penetration of the Cr^{VI} and stops the electron transfer [11,80–82]. As a result, removal of Cr^{VI} in $\text{Fe}^0/\text{H}_2\text{O}$ systems via direct reduction with Fe^0 should, theoretically, have a very low efficiency [83–86]. Nevertheless, the long-term efficiency of $\text{Fe}^0/\text{H}_2\text{O}$ systems for Cr^{VI} removal in reactive walls has been undoubtedly demonstrated [9]. In recent years, several studies have attempted to predict and/or rationalize this observation. Possible reasons included: (1) auto-reduction of atmospheric non-conductive corrosion products yielding electronic conductive magnetite [64,65]; (2) conversion of ferrous hydroxides on Fe^0 to electronic conductive magnetite via the Schikorr disproportionation reaction at $\text{pH} > 6.0$ [87]; and (3) the existence of fissures/defects in the oxide layers, which may initiate pitting corrosion, and allow thus the penetration of Cr^{VI} to Fe^0 core [85,88]. However, it is certain that the effectiveness of Cr^{VI} removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems cannot be ascribed to such processes since: (1) theoretically, for the direct reduction with Fe^0 to occur, the oxide scale should be electronic conductive; however, it was demonstrated that even electron transfer through electrically conductive magnetite occurs at a much lower rate than on the bare Fe^0 surface [87]; therefore, even after the

coating of Fe^0 by magnetite, a reduction of the contaminants may become negligible [89]; and (2) pitting is usually initiated by the presence of important concentrations of aggressive anions (e.g., Cl^-), which are not usually found in natural aquatic environments. In addition, the longer diffusion path to the bottom of the pit restricts the transport of aqueous oxidants from the bulk solution [85]. Therefore, a reasonable explanation for quantitative Cr^{VI} reduction in the $\text{Fe}^0/\text{H}_2\text{O}$ system should be given. The importance of indirect reduction is obvious but the paramount goal of decontamination is removal and not simple reduction. Obviously, since iron oxide layers are excellent adsorbents for negatively charged Cr^{VI} , adsorption of Cr^{VI} onto the oxide layer is the first step that should be taken into account when discussing Cr^{VI} removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems [14,90]. Despite being adsorbed, indirect reduction of Cr^{VI} is still likely. This evidence was taken as example by Noubactep [80] but is still largely ignored in the scientific literature [83,91–93]. Another argument put forward to rationalize Cr^{VI} reduction in $\text{Fe}^0/\text{H}_2\text{O}$ systems is the prevalence of secondary Fe^{II} -bearing mineral phases formed as Fe^0 corrosion products. Enumerated minerals include ferrous sulfides, magnetite, malinawite, siderite, or green rust [6,9,55,94,95]. Even though reduction of Cr^{VI} at the surface of secondary mineral layers was initially believed to be slow [88], recent studies revealed that, actually, Cr^{VI} may be rapidly sequestered at the surface of Fe^{II} -bearing minerals containing structural Fe^{II} and/or Fe^{II} impurities, following an adsorption-reduction mechanism [96,97]. Cr^{VI} adsorption onto positively charged iron and/or chromium oxyhydroxide layers surrounding Fe^0 particles was regarded not only as an intermediate step, but also as an important Cr^{VI} removal mechanism by itself [98–101]. It has been shown that adsorption processes may contribute not only to the removal of Cr^{VI} , but also to the removal of the resulted Cr^{III} [61,86,92]. For instance, XPS analysis carried out on reacted Fe-Ni nanoparticles revealed that ratio between adsorbed Cr^{III} and Cr^{VI} was 7.87 [92]. Therefore, in addition to the heterogeneous reduction mechanism occurring at the surface of Fe^0 , dissolved Fe^{II} and H/H_2 , both products of Fe^0 corrosion, may also be involved in the mechanism of Cr^{VI} removal in $\text{Fe}^0/\text{H}_2\text{O}$ system [62,67,86,91,102–108]. Even though these reduction pathways have been suggested much earlier by several pioneering works in this field [15,18,21], they were often overlooked in articles describing the removal of Cr^{VI} with Fe^0 -based PRBs, as well as in numerous more recent papers. Instead, there are also several recent studies that have clearly indicated that dissolved Fe^{II} should also be taken under consideration as an important reductant of Cr^{VI} . In a study that investigated Cr^{VI} removal by Fe^0 in the presence of organic and inorganic complexing reagents it was revealed that, while EDTA and NaF enhanced the process, 1,10-phenantroline dramatically decreased Cr^{VI} removal [108]. While the favoring effect of EDTA and NaF was ascribed to reduced passivation of Fe^0 due to complexation of Cr^{III} and Fe^{III} , the hindering influence of 1,10-phenantroline was attributed to its well-known specific ability to form a stable complex with Fe^{II} . These outcomes indicated that Cr^{VI} reduction with Fe^{II} was the primary mechanism of Cr^{VI} removal with Fe^0 , rather than Cr^{VI} reduction with Fe^0 [108]. The results of two recent studies reveal that weak magnetic field (WMF) applied during Cr^{VI} removal with Fe^0 significantly improved the efficiency of the process; this phenomenon was ascribed to the enhancement of Fe^0 corrosion process and acceleration of Fe^{II} generation [106,109]. Over the pH range of 4.0–5.5, the highest Cr^{VI} removal rate was observed at pH 5.0. In contrast, the removal rate was limited at pH 4.0 and 5.5 due to slow reaction between Cr^{VI} and Fe^{II} , and slow Fe^{II} generation rate, respectively. Furthermore, Fe^{II} was not detected until Cr^{VI} was completely exhausted, which means that all Fe^{II} released from Fe^0 corrosion was instantaneously oxidized by Cr^{VI} . In the light of all these observations, it was concluded that homogeneous reduction with dissolved Fe^{II} was the main mechanism and the limiting step of Cr^{VI} removal [106]. In a work that studied the influence of humic acids (HA) and fulvic acids (FA) co-presence on the efficiency of Cr^{VI} removal with Fe^0 , higher yields were observed with HA than with FA. Since the concentration of free Fe^{II} was much higher in the HA solutions compared to the FA solutions, the better Cr^{VI} reduction rates observed in the co-presence of HA were ascribed to a greater contribution of the indirect Cr^{VI} reduction with Fe^{II} to the overall removal process [110]. Liu et al. [111] have investigated the effect of citric acid co-presence and of photoirradiation on Cr^{VI} removal with Fe^0 ; it was observed that Cr^{VI} removal efficiency was

not improved in the presence of citric acid, while introduction of photoirradiation in the presence of citric acid dramatically increased the reduction rate of Cr^{VI} . This enhanced efficacy was ascribed to the formation of Fe^{III} -citric acid complexes, which prevented Fe^0 passivation. Moreover, under the effect of photoirradiation, Fe^{III} was reduced to Fe^{II} which, subsequently, homogeneously reduced Cr^{VI} [111]. Last but not least, another possible removal pathway that was recently suggested in the $\text{Fe}^0/\text{H}_2\text{O}$ system is via co-precipitation (entrapment) of Cr^{VI} in the structure of growing Cr^{III} - Fe^{III} oxyhydroxides [90,112–114].

Summarizing, the mechanism of Cr^{VI} removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems generally involves multiple pathways including: (1) adsorption of Cr^{VI} onto Fe^0 or onto oxide layers existent at surface of Fe^0 ; (2) heterogeneous reduction of Cr^{VI} with Fe^0 or, most probably, with Fe^{II} -bearing secondary minerals coated on Fe^0 ; (3) homogeneous reduction of Cr^{VI} with Fe^{II} and/or H_2 ; (4) precipitation of mixed Cr^{III} - Fe^{III} oxyhydroxides; and (5) adsorption/co-precipitation/entrapment of Cr^{VI} on/with/in Cr^{III} - Fe^{III} oxyhydroxides.

3.6. Summary and Conclusions

The conclusions to this section include several important components. First, both laboratory studies and field implementation of PRBs have proven that Fe^0 -based PRBs may be a cost-effective and efficient approach for the remediation of Cr^{VI} polluted groundwater. Second, the efficiency of in situ remediation processes using Fe^0 -based PRBs is influenced mainly by the nature and concentration of contaminant species, nature of reactive mixture (type of Fe^0 , co-presence of adjuvants), and site-specific geochemistry. Third, the presence of a PRB affects not only the concentration of the targeted pollutant(s), but also, to some extent, the concentration of all major dissolved species. Fourth, remarkable progress was made in regard to the understanding of the mechanism of Cr^{VI} removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems; in addition to the direct reduction mechanism, new pathways were indicated including adsorption and indirect reduction with secondary reducing agents (dissolved Fe^{II} , adsorbed Fe^{II} , Fe^{II} -bearing minerals, H_2) produced as a result of Fe^0 corrosion.

4. Geochemistry of Chromium in the Context of Fe^0 -Based Filtration Systems

This section summarizes knowledge from the geochemistry of chromium that is relevant for the understanding of interactions in $\text{Fe}^0/\text{Cr}^{\text{VI}}/\text{O}_2/\text{H}_2\text{O}$ systems. This effort encompasses investigations on the redox reactivity of Cr^{VI} and Fe^{II} -bearing minerals (e.g., Fe_3O_4 or green rusts), as Cr is used also as a chemical surrogate for Tc (the rationale for this being that based on thermodynamic data (E values) Cr reduction occurs before the Tc reduction) [115].

4.1. Geochemistry of Chromium

Chromium is usually encountered in the environment at oxidation states of (+III) and (+VI), which are the most stable from a thermodynamic standpoint. These two chromium species display totally different chemical and toxicological properties [4,116,117]. Under environmentally circumneutral relevant pH values, Cr^{VI} exists only as hydrogen chromate (HCrO_4^-) and chromate (CrO_4^{2-}) oxyanions; at pH values below 6.5 the HCrO_4^- anion is predominant, while at pH above 6.5 the CrO_4^{2-} ion dominates. Cr^{VI} species are highly soluble and therefore easily transported in water resources. In contrast, aqueous Cr^{III} occurs primarily as cationic ($\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$) or neutral ($\text{Cr}(\text{OH})_3^0$) species [5,115,118,119]. Cr^{III} tends to be extremely insoluble (<20 $\mu\text{g}/\text{L}$) between pH 7.0 and pH 10.0, with minimum solubility at pH 8.0 of about 1 $\mu\text{g}/\text{L}$. Hence, Cr^{III} is readily immobilized at circumneutral pH by precipitation as hydroxides, having thus a much lower mobility than Cr^{VI} [14]. Since Cr^{VI} readily crosses cell membranes, it is highly toxic to most living organisms [4]. Cr^{VI} compounds are well-established human carcinogens by the inhalation route of exposure; in addition, Cr^{VI} exposures through drinking water are also likely to be carcinogenic to humans [120–122]. On the contrary, Cr^{III} compounds are poorly transported across membranes, and therefore, toxicity of Cr^{III} is 500 to 1000 times less to a living cell than Cr^{VI} [123,124]. Additionally, Cr^{III} is recognized as a micronutrient

essential for the metabolism of lipids and proteins, being also involved in the biological activity of insulin [125,126].

4.2. Chromium Removal by Fe^{II} Species

Cr^{VI} removal by reduction to Cr^{III} with ferrous iron (Fe^{II}_(aq) or Fe^{II}-bearing minerals including Fe₃O₄, FeS₂ and green rusts) and subsequent adsorption, precipitation, co-precipitation, or coagulation is well documented [5,6]. The following mechanism of Cr^{VI} removal by Fe^{II} is widely accepted in the geochemical literature: (1) Cr^{VI} is reduced to Cr^{III} by Fe^{II}; (2) Fe^{II} is oxidized to Fe^{III}; and (3) Fe^{III} rapidly precipitates as hydroxide. The reduced Cr^{III} is easily adsorbed or co-precipitated with the ferric hydroxide [10,127]. While this view corroborates thermodynamic data, it is still to be made convincing why quantitative Cr^{VI} reduction should precede adsorption. This concern is sustained by the fact that cationic Cr^{III} adsorption onto the positively charged surface of iron oxides and oxyhydroxides at pH values higher than 4.0 is not always favorable (depending on the specific (hydr)oxide). As an example, under subsurface conditions where magnetite (Fe₃O₄, p*H*_{pzc}~5.0) is the major mineral, the Fe₃O₄ surface is positively charged at pH < 5.0; therefore, anionic soluble Cr^{VI} species are expected to be strongly attracted via electrostatic interactions. For pH > 5, more negatively charged surfaces are developed, further reducing the attraction of Cr^{VI} species [5,115]. However, some quantitative adsorption may still occur, suggesting inner-sphere adsorption mechanisms via ligand exchange reactions [115]. A more rationale view is that negatively charged Cr^{VI} species are adsorbed onto positively charged Fe (hydr)oxides and reduction occurs in an adsorbed state [128]. The very low solubility of Cr^{III} phases implies that quantitative re-dissolution will not occur. Moreover, the formation of Fe^{III}/Cr^{III} mixed (hydr)oxides further decreases the solubility of the solid phase.

4.3. Overview of Reactions of Engineering Importance

Under environmental conditions, virtually all transformations from Cr^{VI} to Cr^{III} and vice versa are mediated by constituents that are ubiquitous in nature. Depending mostly on the water flow velocity (i.e., on contact time) and on the intrinsic reactivity of Fe^{II}-bearing phases, interactions with contaminated water may not achieve an equilibrium state. In such cases, kinetics of the transformations between Cr^{VI} and Cr^{III} become important [5]. Chemical reduction of Cr^{VI} to Cr^{III} is a demonstrated path for Cr removal in many water treatment strategies. Ideally, Cr^{VI} reduction is followed by precipitation of the soluble Cr^{III} species to particulate Cr(OH)₃ or adsorbed solids (flocs) that can be filtered from the water. The most common reducing agent is Fe^{II}, with reaction times on the order of seconds to hours, depending on pH [5]. The state-of-the-art knowledge from the chromium geochemistry can be summarized by the following two-step mechanism of Cr^{VI} removal at Fe₃O₄ surface [129]: (1) electrostatic adsorption of Cr^{VI} anions at Fe₃O₄ surface; and (2) the electron transfer reaction between Cr^{VI} and the structural Fe^{II} to form Cr^{III}(OH)₃. The Cr^{VI} reduction is accompanied by simultaneous homogenous oxidation of Fe^{II} to Fe^{III}. Nascent Fe^{III} hydroxides are powerful adsorbing and enmeshing agents for Cr^{VI}. Due to similarities in atomic size, Fe and Cr form mixed oxides that are non-conductive for electrons and yield to passivation of magnetite. Accordingly, Cr^{VI} reduction by Fe₃O₄ is rarely quantitative (e.g., >70%). The removal mechanisms suggested by Kendelewicz et al. [129] is valid under a wide range of reaction conditions, despite difference in Cr speciation, pH values, background electrolyte and changes of the adsorbing surface charge [115]. It can be postulated that its validity does not depend on the nature of the Fe^{II}-bearing material, and, in particular, that it will still be valid if Fe^{II} results from Fe⁰ oxidative dissolution (Fe⁰ corrosion).

5. Recent Advances

5.1. Analysis of the Fe⁰/Cr^{VI}/O₂/H₂O System

Aqueous Cr^{VI} removal in the presence of Fe⁰ depends primarily on the chemical thermodynamics of five redox systems (Table 1): (1) Fe^{II}/Fe⁰ (Equation (19)); (2) Cr^{VI}/Cr^{III} (Equations (20) and (25));

(3) H^+/H_2 (Equation (21)); (4) Fe^{III}/Fe^{II} (Equation (22)); and (5) O_2/HO^- (Equation (23)). Both the aqueous solution behavior and the redox thermodynamics are of interest. In addition, the reactions kinetics is a decisive factor for the design of remediation systems [130,131].

Table 1. Relevant electrode reactions for the discussion of processes occurring in $Fe^0/Cr^{VI}/O_2/H_2O$ system. To ease readability some equations are repeated here with new numbers.

Electrode Reaction	E^0 (V)	Eq.	Reference
$2H_2O + 2e^- \rightleftharpoons H_2 + 2HO^-$	-0.83	(17)	[132]
$Cr^{3+} + 3e^- \rightleftharpoons Cr^0$	-0.74	(18)	[132]
$Fe^{2+} + 2e^- \rightleftharpoons Fe^0$	-0.44	(19)	[132]
$CrO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Cr(OH)_3 + 5OH^-$	-0.13	(20)	[132]
$2H^+ + e^- \rightleftharpoons H_2$	0.00	(21)	[132]
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.77	(22)	[132]
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4HO^-$	0.40	(23)	[132]
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.23	(24)	[132]
$HCrO_4^- + 7H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O$	1.35	(25)	[132]
Electrochemical reactions (involving Fe^0)			
$3Fe^0 + 2CrO_4^{2-} + 8H_2O \rightleftharpoons 3Fe^{2+} + 2Cr(OH)_3 + 10 OH^-$		(26)	[6]
$Fe^0 + 2H_2O \rightleftharpoons Fe^{2+} + H_2 + 2HO^-$		(27)	[6]
$Fe^0 + 2Fe^{3+} \rightleftharpoons 3Fe^{2+}$		(28)	[25]
$2Fe^0 + O_2 + 2H_2O \rightleftharpoons 2Fe^{2+} + 4OH^-$		(29)	[29]
Chemical reactions			
$4Fe^{2+} + O_2 + 2H_2O \rightleftharpoons 4Fe^{3+} + 4OH^-$		(30)	[27]
$3Fe^{2+}_{ads} + CrO_4^{2-} + 8H_2O \rightleftharpoons Cr(OH)_3 + 3Fe(OH)_3 + 4H^+$		(31)	[133]
$2Cr(OH)_2^+ + 3/2O_2 + H_2O \rightleftharpoons 2CrO_4^{2-} + 6H^+$		(32)	[134]
$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$		(33)	[135]
$HCrO_4^- + H_2O \rightleftharpoons CrO_4^{2-} + H_3O^+$		(34)	[135]
$HCrO_4^- + HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$		(35)	[135]
$[Cr(OH_2)_6]^{3+} + H_2O \rightleftharpoons [Cr(OH_2)_5(OH)]^{2+} + H_3O^+$		(36)	[135]
$[Cr(OH_2)_5(OH)]^{2+} + H_2O \rightleftharpoons [Cr(OH_2)_4(OH)_2]^+ + H_3O^+$		(37)	[135]
$[Cr(OH_2)_4(OH)_2]^+ + H_2O \rightleftharpoons [Cr(OH_2)_3(OH)_3] + H_3O^+$		(38)	[135]
$[Cr(OH_2)_3(OH)_3] + H_2O \rightleftharpoons [Cr(OH_2)_2(OH)_4]^- + H_3O^+$		(39)	[135]
$2Cr^{3+} + 2H_2O \rightleftharpoons Cr_2(OH)_2^{4+} + 2H^+$		(40)	[136]
$3Cr^{3+} + 4H_2O \rightleftharpoons Cr_3(OH)_4^{5+} + 4H^+$		(41)	[136]
$4Cr^{3+} + 6H_2O \rightleftharpoons Cr_4(OH)_6^{6+} + 6H^+$		(42)	[136]
$(1-x)Fe^{3+} + (x)Cr^{3+} + 2H_2O \rightleftharpoons Cr_xFe_{1-x}(OOH) + 3H^+$		(43)	[76]
$(1-x)Fe^{3+} + (x)Cr^{3+} + 3H_2O \rightleftharpoons Cr_xFe_{1-x}(OH)_3 + 3H^+$		(44)	[76]

In the context of water treatment by granular Fe^0 , the negative potential of the redox couple Fe^{II}/Fe^0 (Equation (19)) is to be exploited to transform the highly soluble Cr^{VI} into sparingly soluble Cr^{III} in an electrochemical process (Equation (26)). Further electrochemical processes include the reduction of water (Equation (27)), Fe^{III} (Equation (28)) and dissolved O_2 (Equation (29)) with Fe^0 . Of these, only water reduction (Equation (27)) is likely to be quantitative because of the non-conductive nature of the oxide scale and its role as a physical barrier. Equation (28) is disfavored by the low solubility of Fe^{III} species. There are myriad abiotic chemical reactions likely to occur in Fe^0/H_2O systems (Equation (30) through Equation (44)). Equation (30) accelerates Fe^0 corrosion by consuming Fe^{2+} (LeChatelier) and thus increasing the production of iron oxides/hydroxides for Cr^{VI} adsorption and co-precipitation. Equation (31) sustains the chemical reduction of adsorbed Cr^{VI} ; it is not a reductive precipitation, but a reduction of adsorbed Cr^{VI} . This reaction path is not necessarily quantitative. Equation (32) is slow with soluble $Cr(OH)_3$ and impossible with $Cr(OH)_3$ generated in an adsorbed state. Equations (33)–(35): concentrations of Cr^{VI} species depends on pH and total Cr concentration; significant concentrations of H_2CrO_4 occur only at $pH < 1$. $Cr_2O_7^{2-}$ becomes significant when Cr^{VI} concentrations are > 1 mM, or it may even dominate when Cr^{VI}

concentrations are > 30 mM [137]. Equations (36)–(39) shows that Cr^{III} is a hard Lewis acid with a high tendency to undergo hydrolysis [138]. Equations (40)–(42): because in most natural waters the aqueous concentration of Cr^{III} is very low, and the kinetics of polymerization are slow under environmentally relevant pH and temperature values, polymeric Cr^{III} species are never significant in natural unpolluted aquatic systems [116,119,138]. Equations (43) and (44) describe the formation of mixed (oxy)hydroxides within $\text{Fe}^0/\text{H}_2\text{O}$ systems, process that occurs at pH greater than 4; it was hypothesized that $\text{Cr}_{0.25}\text{Fe}_{0.75}(\text{OH})_3$ will form if Fe^{III} and Cr^{III} are generated only by the reaction between Fe^{II} and Cr^{VI} [76,119,137]. Summarizing, the analysis of the $\text{Fe}^0/\text{Cr}^{\text{VI}}/\text{O}_2/\text{H}_2\text{O}$ system suggests that adsorption of negatively charged $\text{HCrO}_4^-/\text{CrO}_4^{2-}$ onto positively charged iron (hydr)oxides is the most likely reaction path. This high affinity coupled to the barrier function of the oxide scale implies that “reductive precipitation” is at most a side removal path.

5.2. The Mechanism of Cr^{VI} Removal Revisited

Knowledge from: (1) the chromium geochemistry (Section 4); and (2) the theoretical analysis of the $\text{Fe}^0/\text{Cr}^{\text{VI}}/\text{H}_2\text{O}$ system (Section 5.1) univocally prove the reductive precipitation theory for aqueous Cr^{VI} removal in the presence of Fe^0 as being faulty. This corresponds to an alternative concept introduced by Noubactep in 2006 [11,80,114,139–143], but largely ignored within the Fe^0 research community [11,82]. According to Ghauch [82], only some five research groups have tested (and validated) the alternative concept worldwide. The alternative concept argues that the $\text{Fe}^0/\text{H}_2\text{O}$ system is a complex system in which quantitative contaminant reduction, when it occurs, is not the cathodic reaction coupled to the anodic dissolution of Fe^0 . Accordingly, (quantitative) Cr^{VI} reduction in $\text{Fe}^0/\text{H}_2\text{O}$ systems is mediated by Fe^{II} species (and, possible, also by H/H_2) resulting from electrochemical dissolution with water or H^+ . The particularity is that Fe^{II} is continuously produced, while freshly generated iron hydroxides act as excellent adsorbents for Cr^{VI} and Fe^{II} (structural Fe^{II} or $\text{Fe}^{\text{II}}_{(\text{ads})}$). It should be kept in mind that solid structural Fe^{II} seems to be a stronger reducing agent than both dissolved Fe^{II} [128] and Fe^0 . Similarly, innerspherically adsorbed Fe^{II} is also more reducing than dissolved Fe^{II} . All these facts excellently explain the better Cr^{VI} removal efficiency of a Fe^0/sand mixture with iron hydroxides coated on sand, compared to that of Fe^0 alone (same Fe^0 mass) [144].

5.3. Application to Water Filters

The knowledge that Fe^0 is mostly generator of iron hydroxides and oxides, acting as coagulating/adsorbing agents, was already successfully applied in Europe, around the year 1890, for safe drinking water production [12]. However, today available Fe^0 -amended filtering systems are based on a more pragmatic approach. Two examples will be given for illustration: the SONO arsenic filter [145–147] and the Indian Institute of Technology in Bombay (IITB) arsenic filter [148]. It is important to underline here that both filters are not specific for arsenic removal, and would remove Cr^{VI} and other contaminants as well. The first arsenic filtration system (3-Kolshi filter) was developed in 1999 by Abul Hussam and his brother Abul Munir, after two years of research motivated by the need to develop a simple and low cost water treatment system for mitigation of the arsenic crisis in Bangladesh. The 3-Kolshi filter (made entirely from readily local available materials) consisted in three clay containers placed one top of another, with water flowing through a series filters made of sand, iron chips, and wood charcoal. Even though it was successfully tested for its efficacy in removing arsenic from groundwater, the 3-Kolshi filter had a major problem: the rapid clogging of the iron material [149,150]. To solve this issue, the team led by Abul Hussam and Abul Munir released, in 2001, the SONO filter; in this new filtration assembly, the clay containers were replaced by plastic buckets and, most important, iron chips were replaced by a composite iron matrix (mixture of metal iron and iron hydroxides). This technology was patented in 2002 and, by 2010, about 160,000 SONO filters were deployed in Bangladesh, India, and Nepal. Even though SONO filters are not freely accessible to people in need, at a price of \$35–40 (for an expected life span of at least 5 years), and with operating costs up to \$10/5 years, they are one of the most affordable water filters available

today [145,149,150]. The IITB filter is the most recent result of continuous research in the development of a robust, low cost, and simple arsenic removal water treatment system for poor communities in low income areas. It uses non-galvanized iron nails which, under the mild oxidizing environment (presence of dissolved oxygen), are corroded. The formed Fe^{II} is oxidized to Fe^{III} , forming a high oxidizing intermediate which co-oxidizes As^{III} to As^{V} ; subsequently As^{V} is adsorbed on the corrosion products existent at the surface of Fe^0 . Along with a high performance for removing arsenic, this technology also has the advantage that the Fe^0 requirement is 20 times less than similar arsenic removal efficiencies reported in the literature for other methods. The IITB filter is a non-patented system designed for small communities. Its implementation started in 2008 and there are already some 60 systems working under maintenance of the rural population in India (mostly in West Bengal) [150].

The most important concern of Fe^0 -based filters is related to permeability loss (reduction of the hydraulic conductivity), which leads to an incomplete utilization of Fe^0 [26]; the long-term permeability can be prolonged only if the volumetric expansion of iron corrosion products (which is the main cause of permeability loss) is properly considered during the design of Fe^0 -based filters [151]. The two examples considered herein have differently solved the clogging problem. On the one hand, SONO filters used a composite iron matrix with high initial porosity, capable to store the iron corrosion products [145]. On the other hand, IITB filters perform a sort of flocculation in a contactor placed on top of the filter, where the water is contacted with iron nails and with air. Subsequently, the formed hydrous ferric oxide floccules are filtered on a fixed-bed filled with layers of coarse and fine gravel. During this process, the oxidation of Fe^{II} to Fe^{III} and As^{III} to As^{V} occurs. This configuration shows that the IITB filter can be regarded as a modification of the revolving purifier (Anderson Process) [12,152] with the added advantage that no revolution is needed and the system can operate energy free.

According to 2017 World Health Organization Joint Monitoring Programme Report, 844 million people still lacked a basic drinking water service; this includes 263 million people who spend over 30 min to collect water from sources outside the home, and 159 million people collected drinking water directly from surface water sources (58% lived in sub-Saharan Africa) [153]. Since Fe^0 -amended filters were successfully tested in the battle against arsenic poisoning in southern Asia, they may also offer a unique opportunity to solve the worldwide shortage for safe drinking water provision on a self-reliant manner.

6. Concluding Remarks

The mechanism of contaminant removal in Fe^0 -based systems and the identity of the redox active species involved in the mechanism were the subject of an active debate in the last years. The first concept proposed in the early nineties for the removal of Cr^{VI} with Fe^0 , and widely accepted since then, was the reductive-precipitation mechanism. This concept attributed the efficiency of $\text{Fe}^0/\text{H}_2\text{O}$ systems to Cr^{VI} chemical transformations, mainly to direct reduction with Fe^0 and subsequent (co-) precipitation of the resulted cations. Recently, a new approach (the adsorption-co-precipitation concept), provided added perspectives to the mechanism of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems, trying to demonstrate that direct reduction (if applicable) is less important than had previously been assumed. According to this new concept, contaminants are quantitatively removed in $\text{Fe}^0/\text{H}_2\text{O}$ systems principally by adsorption and co-precipitation, while reduction, when possible, is mainly the result of indirect reducing agents produced by Fe^0 corrosion. Based on the current knowledge, this review clearly demonstrates that Cr^{VI} removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems is actually a very complex mechanism, including the adsorption, reduction, and co-precipitation/entrapment processes. Therefore, the new adsorption-co-precipitation concept should not be considered as a contradiction, but as an extension to the reductive-precipitation theory.

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