# Aqueous contaminant removal by metallic iron: Is the paradigm shifting?

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#### Abstract

Chemical reduction has long dominated thinking about the mechanism of aqueous contaminant removal in the presence of metallic iron (e.g.  $Fe^0/H_2O$  systems). However, a large body of experimental evidence indicates that chemical reduction is not adequate to satisfactorily explain the efficiency of  $Fe^0/H_2O$  systems for several substances or classes of substances. By contrast, the alternative approach, that contaminants are fundamentally adsorbed and co-precipitated by iron corrosion products seems to provide a better explanation of observed efficiency. The new approach appears to not be fully understood. The present communication aims at clarifying this key issue. It seems that a paradigm shift is necessary for the further development of the technology using  $Fe^0$  for water treatment.

Keywords: contaminant removal, paradigm shift, removal mechanism, water treatment, zero-valent iron

#### Introduction

The publication by Thomas Kuhn (1962) of his book *The Structure of Scientific Revolutions* was the starting point for the frequent use of the word 'paradigm' in many fields of science. Kuhn characterised a paradigm as a shared theory of the nature of something or of how it operates, together with a related set of problems to be solved and a kit of tools or methods for approaching those problems (Heaney, 2003; Rowbottom, 2011). Researchers introduced into a field, learned about the paradigm. Their challenge is to apply some tools of the prevailing paradigm to clarify some of its unsolved problems. For the field of water treatment with metallic iron (Fe<sup>0</sup>), it is safe to say that contaminant reduction by Fe<sup>0</sup> constitutes the basis of its operative paradigm.

Since the introduction of Fe<sup>0</sup> for water treatment in 1990 (Reynolds et al., 1990; Gillham and O'Hannesin, 1994), contaminants have been reported to be removed by reductive transformations (Matheson and Tratnyek, 1994; Weber, 1996; O'Hannesin and Gillham, 1998; Comba et al., 2011). Clearly, contaminants were considered to be removed because of their chemical transformations possibly making them less harmful (degradation) or less mobile (precipitation). Accordingly, the case for which contaminant reduction products may be more toxic than parent contaminants (e.g.  $CCl_{4}$ ) is still actively discussed (Jiao et al., 2009; Alvarado et al., 2010). Moreover, the formation of the universal oxide film on the Fe<sup>0</sup> surface (reactivity loss) and the pore filling by iron corrosion products (permeability loss) have been regarded as the major inhibitive factors for the process of contaminant removal (Henderson and Demond, 2007; Ghauch, 2008a; Simon et al., 2008; Li and Benson, 2010). Accordingly, 3 major problems of the Fe<sup>0</sup>

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e-mail: <u>cnoubac@gwdg.de</u> Received 27 September 2010; accepted in revised form 30 May 2011. technology thus introduced are:

- How can harmful reaction products be removed?
- How can reactivity loss be prevented?
- How can permeability loss be properly considered?

Several analytical tools and complicated experimental devices has been used over the past 2 decades to search for answers to these 3 questions (Wilderer et al., 2002; McGuire et al., 2003; Simon et al., 2004). Even today, a cursory survey of the literature on Fe<sup>0</sup> technology will find, in the introduction to virtually every paper, phrases such as '... Fe<sup>0</sup> is proved to be particularly suitable for the decontamination of halogenated organic compounds, but subsequent studies have confirmed the possibility of using Fe<sup>0</sup> for the reduction of nitrate, bromated, chlorate, nitro aromatic compounds, brominated pesticides. Fe<sup>0</sup> proved to be effective in removing arsenic, lead, uranium and hexavalent chromium..." (Groza et al., 2009). It is important to notice that 'contaminant reduction' and 'contaminant removal' are mostly randomly interchanged.

It should be explicitly stated that some researchers have insisted on the importance of adsorption and/or co-precipitation in the process of aqueous contaminant removal by Fe<sup>0</sup> (Burris et al., 1995; Allen-King et al., 1997; Lackovic et al., 2000; Lavine et al., 2001; Furukawa et al., 2002; Ritter et al., 2002; Wilkin and McNeil, 2003; Su and Puls, 2004; Mielczarski et al., 2005). However, their arguments were limited to inorganic contaminants (e.g. Lackovic et al., 2000; Wilkin and McNeil, 2003), to selected organic species (e.g. Mielczarski et al., 2005), or to investigations on the impact of iron corrosion products as contaminant scavengers (Furukawa et al., 2002; Jia et al. 2007) or reducing agents (Refait et al., 1998; Ritter et al., 2002; O'Loughlin et al., 2003; O'Loughlin and Burris, 2004; Chaves, 2005 ; Liang and Butler, 2011). For example, Furukawa et al. (2002) stated that under oxic conditions, ferrihydrite may be one of the most abundant iron corrosion products and may play an important role in adsorbing contaminants. In such situations, the use of Fe<sup>0</sup> reactive walls 'may be extended to applications that require contaminant adsorption rather than, or in

Table 1Overview of important results of the first 4 published peer-reviewed articles on the Feº/H 2Osystem (1994) and the number of citations of these as reported by Scopus (27 March 2011).It can be seen that none of these seminal works has demonstrated quantitative contaminant reduction. Moreover, the least cited work is the one which has created conditions for favourable contaminant reduction (acidification by FeS2). X stands for contaminant; RCI is a chlorinated hydrocarbon.				
Reference	Systems	x	Findings	Citations
Matheson and Tratnyek	Fe <sup>0</sup> /H <sub>2</sub> O	CH <sub>x</sub> Cl <sub>y</sub>	Degradation mostly by Fe <sup>0</sup>	616
Gillham and O'Hannesin	Fe <sup>0</sup> /H <sub>2</sub> O	RCl	Enhanced degradation	597
Schreier and Reinhard	Fe <sup>0</sup> /H <sub>2</sub> O	C <sub>2</sub> Cl <sub>4</sub>	Partial degradation	65
Lipczynska-Kochany et al.	Fe <sup>0</sup> /FeS <sub>2</sub> /H <sub>2</sub> O	CCl4	FeS <sub>2</sub> accelerates degradation	49

addition to, redox-promoted contaminant degradation'. On the other hand, the findings of Lackovic et al. (2000) that arsenic is not removed by a reductive transformation process were clearly presented as an exception. It is important to note that results from the very first peer-reviewed articles on the Fe<sup>0</sup>/H<sub>2</sub>O systems were uncertain about the real mechanisms of contaminant removal (Table 1). However, the hypothesis of contaminant reduction was favoured without experimental evidence (e.g. mass balance) (e.g. Lee et al., 2004). As stated by O'Hannesin and Gillham (1998), it was a 'broad consensus'.

The kit of tools to investigate contaminant reduction includes a large number of highly sophisticated instruments for determining contaminant concentration and speciation, identifying contaminant reaction products and iron corrosion products as well (McGuire et al., 2003). Tools further used aimed at properly modelling experimental data and thus design field Fe<sup>0</sup> treatment units (e.g. field reactive walls, household filters) (Schüth et al., 2003; VanStone et al., 2005; Li et al., 2006; Kouznetsova et al., 2007: Klammler and Hatfield, 2008: Li and Benson, 2010; Jeen et al., 2011). Additionally, researchers were organised in networks (e.g. PRBT - the US Permeable Reactive Barriers Action Team; RUBIN - the German Permeable Reactive Barrier Network; PRB-Net - the Permeable Reactive Barrier Network in the United Kingdom) having the goal to accelerate the development of the promising Fe<sup>0</sup> technology. Thus, it would seem that the role of reductive transformation in the process of contaminant removal by Fe<sup>0</sup> fulfils all of the criteria for a true paradigm.

It should be acknowledged that the reductive transformation concept has been a fruitful paradigm, fuelling substantial progress for the achieved acceptance of the Fe<sup>0</sup> technology (Bigg and Judd, 2000; Scherer et al., 2000; Henderson and Demond, 2007; Laine and Cheng, 2007; Cundy et al., 2008; Thiruvenkatachari et al., 2008; Groza et al., 2009; Muegge and Hadley, 2009; Gillham, 2010; Phillips et al., 2010). Nevertheless, a growing body of evidence indicates that factors other than reductive transformations contribute importantly to the process of contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O systems. These factors included adsorption, co-precipitation and adsorptive size exclusion.

#### Limits of the reductive transformation concept

Concordant reports on enhanced Fe<sup>0</sup> reactivity towards aqueous contaminant removal with decreasing particle size have been reported. As a consequence, nano-scale Fe<sup>0</sup> (nano-Fe<sup>0</sup>) has been suggested and is currently injected into the subsurface for groundwater remediation (Wang and Zhang, 1997; Comba et al., 2011; Shi et al., 2011). Another common tool to enhance Fe<sup>0</sup> reactivity is the use of bimetallic materials (Fe/Cu, Fe/ Ni, Fe/Pd) (Muftikian et al., 1995). However, neither the use of nano-Fe<sup>0</sup> (Noubactep and Caré, 2010a) nor that of bimetallic systems (Noubactep, 2009a) is consistent with the fact that contaminants should be reduced by Fe<sup>0</sup>. While the plating metals (e.g. Cu<sup>0</sup>, Ni<sup>0</sup>, Pd<sup>0</sup>) are concurrent reagents for Fe<sup>0</sup> oxidation, nano-Fe<sup>0</sup> will be readily oxidised by water which is in stoichiometric excess relative to dissolved contaminants. Both of these facts ('anomalies') are the first arguments against the view that contaminants are quantitatively removed by reductive transformations.

Several other experimental results seem to have stretched the reductive transformation paradigm to the point where it may no longer be intellectually satisfying. Among these results (Noubactep, 2007; Noubactep, 2010a; Scott et al., 2011 and references cited therein) are:

- The quantitative removal of species like Zn<sup>II</sup> which is not reducible by Fe<sup>0</sup> or the quantitative removal of Mo<sup>VI</sup> which is not readily adsorbed on iron oxides (at pH > 6)
- The quantitative removal of organic species in Fe<sup>0</sup> beds which were proven as non-reducible by Fe<sup>0</sup> in batch systems (Lai et al., 2006)
- The existence of the lag time in the process of contaminant removal in batch systems (Schreier and Reinhard, 1994; Hao et al., 2005).

Where the reductive transformation paradigm is not useful, researchers have favoured selective adsorption or microbial processes to explain observed results (Lai et al., 2006). However, this approach can be regarded as a falsification of the reductive transformation paradigm since it assumes that adsorption is only important when reduction is not favourable. Moreover, contaminant co-precipitation with precipitating and transforming iron oxides is considered only for specific cases, as discussed above. This is the juncture (proliferation of anomalies) at which Kuhn observes that paradigms tend to shift (Heaney, 2003).

The expression 'paradigm shift' is believed to be misused or overused in science. For this reason, this communication proposes that the reductive transformation paradigm is giving way to a successor that seems to provide an operationally superior and intellectually more attractive rationalisation of the process of aqueous contaminant removal by Fe<sup>0</sup>.

It must be acknowledged that the principle that contaminants are quantitatively removed in Fe<sup>0</sup>/H<sub>2</sub>O systems has never been in question. The sole discussion is about the occurrence of reduction (if applicable) and its extent (Lee et al., 2004). The next section will briefly present a different view on the process of contaminant removal which is the essence of the alternative paradigm. The new concept suggests an analogy with the historical work of Yao et al. (1971) that contaminants are collected in Fe<sup>0</sup> beds (deep bed filters) by *in situ* generated Fe<sup>II</sup>/Fe<sup>II</sup>-species, regardless of whether they are chemically transformed or not.

### Adsorption/co-precipitation concept

The concept that contaminants are fundamentally adsorbed and/or co-precipitated onto/with iron corrosion products in Fe<sup>0</sup>/ H<sub>2</sub>O systems has been extensively presented in several recent articles (e.g. Noubactep, 2010a; 2010b). The concept arose from a fortuitous observation during experiments on the process of uranium removal in 'Fe<sup>0</sup>/MnO<sub>2</sub>/H<sub>2</sub>O' systems ('Fe<sup>0</sup>', 'MnO<sub>2</sub>' and 'Fe<sup>0</sup> + MnO<sub>2</sub>') (Noubactep et al., 2003) and is supported by results from all other branches of science involving aqueous iron corrosion (Noubactep, 2009b; Noubactep and Schöner, 2009; Noubactep and Schöner, 2010).

In the mentioned experiments,  $MnO_2$  and waterworks sludge (aged iron oxides –  $Fe_2O_3$ ) were used as relevant adsorbents and their impact on the process of U<sup>VI</sup> removal by Fe<sup>0</sup> was characterised. Results showed that none of the adsorbents could significantly accelerate U<sup>VI</sup> removal. Moreover,  $MnO_2$  essentially retarded U<sup>VI</sup> removal and the lag time was proportional to the available amount of  $MnO_2$ . These results indicated that U<sup>VI</sup> is mostly removed by in-situ generated iron corrosion products. Aged  $Fe_2O_3$  could not significantly impact U<sup>VI</sup> removal.  $MnO_2$ essentially retarded the removal process. This delay is due to the fact that iron hydroxides are not precipitated in the vicinity of Fe<sup>0</sup> but rather at the surface of  $MnO_2$ . The process of reductive dissolution of  $MnO_2$  by Fe<sup>II</sup> is a well-documented geochemical process (Stone, 1987; Stone and Ulrich, 1989; Postma and Appelo, 2000; Kang et al., 2006).

A close consideration of the impact of MnO<sub>2</sub> on the process of U<sup>VI</sup> removal by Fe<sup>0</sup> suggested that U<sup>VI</sup> removal is a characteristic of corroding iron. In other words, UVI removal is not necessarily a reductive process or a result of any specific interactions between UVI and Fe<sup>0</sup>. Specific interactions between contaminants and Fe<sup>0</sup> (and iron oxides) will certainly favour the removal process but are not the determinant factors (Scott et al., 2011). Accordingly, a Fe<sup>0</sup>/H<sub>2</sub>O system can be regarded as a domain of precipitating iron hydroxide (Noubactep, 2009c). In such a system, any inflowing contaminant will be adsorbed and co-precipitated. Additionally, Fe<sup>II</sup> and H/H, from continuously corroding Fe<sup>0</sup> are reducing agents for reducible contaminants in the system but the extent of contaminant reduction is difficult to discuss because generated iron oxides must be digested for contaminant speciation and mass balance calculations. On the other hand, contaminants enmeshed in the matrix of iron corrosion are stable for a long time under environmental conditions, whether they are chemically transformed or not (Noubactep et al., 2006).

The presentation above has explained why all classes of aqueous contaminants may be quantitatively removed by Fe<sup>0</sup>. It is clear from this presentation that parent contaminants and their reaction products are all removed in Fe<sup>0</sup>/H<sub>2</sub>O systems. This is consistent with the view that in a Fe<sup>0</sup> bed *in situ* generated Fe hydroxides and oxides act as contaminant 'collectors' (Yao et al., 1971). Accordingly, one of the 3 major problems introduced (how can harmful reaction products be removed?) by the reductive transformation concept is solved. The remaining 2 problems are:

- How can reactivity loss be prevented?
- How can permeability loss be properly considered?

Answering these questions is beyond the scope of this communication. However, it should be pointed out that recent theoretical works have shown that to sustain system permeability, Fe<sup>0</sup> should be admixed to inert materials in a volumetric ratio of less than 52%. In other words, an efficient Fe<sup>0</sup> bed could be regarded as a Fe<sup>0</sup> amended sand filter. A proposed tool to sustain reactivity is to use Fe<sup>0</sup>/MnO<sub>2</sub> mixtures (Noubactep et al., 2010).

The concept presented in this section clearly underplays the importance of reduction in the process of aqueous contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O systems. There is increasing evidence that this concept is not yet understood by authors who have referenced related papers. The next section will address this issue.

#### Argumentation against the new concept

The concept regarding adsorption and co-precipitation as the fundamental mechanisms of contaminant removal in  $Fe^0/H_2O$  systems has been experimentally validated using methylene blue as model contaminant (Noubactep, 2009d). The concept has recently been verified using clofibric acid (Ghauch et al., 2010a) and diclofenac (Ghauch et al., 2010b). Moreover, the similitude between contaminant removal with elemental metals and electro-coagulation has been excellently presented by Bojic et al. (2004; 2007; 2009). Nevertheless, there are currently 5 types of arguments in the literature downplaying the significance of this concept:

- The concept is wrongly referenced (Luna-Velasco et al., 2010; Yuan et al., 2010) (Argument 1)
- The concept is hardly acceptable because the reductive transformation concept is widely accepted in the scientific community, and self-citation is always used to support the validity of the new concept (Kang and Choi, 2009) (Argument 2)
- Good results on removal of inorganic species by Fe<sup>0</sup> are unacceptably generalised (Ebert et al., 2007; Tratnyek and Salter, 2010) (Argument 3)
- Data are needed to support the repeated claims which negate more than 1 decade of intensive research (Ebert et al., 2007; Tratnyek and Salter, 2010) (Argument 4)
- Some authors who have correctly referenced the adsorption/co-precipitation concept deliberately ignored it in their subsequent publications (Argument 5).

For example, Flury and his colleagues (Flury et al., 2009a; 2009b) referenced Noubactep (2006) in a paper published in *Applied Geochemistry* (available online 24 December 2008) and not in the paper for *Environmental Science & Technology* (accepted May 14, 2009). At the same time, three more recent papers which further elaborated on the new concept were available. In another example, Lo and co-workers correctly referenced the concept in 2008 (Rao et al., 2009; accepted 11 December 2008) but not in several subsequent works (e.g. Liu et al., 2009; Mak et al., 2009; 2011). Short comments on individual arguments are given below.

- Argument 1: The concept was introduced in 2007 in an open access journal (Noubactep, 2007). Therefore, there seems to be no reason why so many researchers would appear to have ignored or wrongly referenced it. Referencing articles using or presenting the new concept, co-precipitation is enumerated as a 'simple' reaction mechanism beside adsorption and reduction (Luna-Velasco et al., 2010; Yuan et al., 2010). That researchers appear to be ignoring state-of-the-art knowledge on the mechanism of contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O systems should be a concern for the whole community.
- Argument 2: The consistency of the concept of reductive transformation has been extensively discussed while

introducing the concept of adsorption/co-precipitation. Researchers should have discussed the validity of the new concept instead of simply expressing doubt as to its validity. Fortunately, Ghauch, who was initially sceptical about the adsorption/co-precipitation concept (Ghauch, 2008b), has experimentally verified its efficiency in explaining processes which are still mistakenly attributed to plated Fe<sup>0</sup> (Ghauch et al., 2010b).

- Argument 3: Not all inorganic substances are readily adsorbed onto iron oxides (iron corrosion products) (Blowes et al., 2000). For example, Mo<sup>VI</sup> is very poorly adsorbed on iron oxides at pH > 6.0 (Scott et al., 2011 and references cited therein) but was reported to be successfully removed by Fe<sup>0</sup> (Morrison et al., 2002; 2006). On the other hand, many organic compounds are readily adsorbed onto iron oxides (Tipping and Higgins, 1982; Tipping, 1986; Gu et al., 1994, Satoh et al., 2006; Hanna and Boily, 2010; Eusterhues et al., 2011). Besides this evidence from the geochemical literature, it has been clearly demonstrated that contaminant removal is not primarily a property of contaminants but rather a characteristic of aqueous iron corrosion. In other words, contaminants are not removed by Fe<sup>0</sup> or Fe oxides separately, but during the whole dynamic process of aqueous iron corrosion. In Fe<sup>0</sup> beds, adsorptive size exclusion in deep bed filtration mode sustains the removal efficiency. The argument of self-citation is not acceptable because nobody else has systematically reported on the inconsistency of the reductive transformation concept. Moreover, authors like Burris et al. (1995), Lavine et al. (2001), Mantha et al. (2001) and Odziemkowski (2009), who have seriously questioned some aspects of the reductive transformation concept, have been continuously referenced.
- Argument 4 is mostly used by reviewers and referees who have rejected several manuscripts and proposals. Rejected manuscripts were subsequently accepted by other reviewers, sometimes from the same journal in a new submission. It is important in this regard to note that many reviewers have argued that the review articles presenting the concept of adsorption/co-precipitation could never have been published in ISI-referenced journals (Noubactep, 2006; 2007) or in journals with higher impact factors (Noubactep, 2008) because of the concept's poor scientific quality. While manuscripts could be revised and re-submitted, proposals have been systematically rejected. This is a well-known situation whenever a new view is introduced (Alm, 1992; Heaney, 2003).
- Argument 5 suggests that the ground-breaking nature of the concept was not clear to the authors who may have been prompted by peer-reviewers to reference related works.

The comments above showed that no single valid argument against the adsorption/co-precipitation concept has yet been presented. Moreover, theoretical studies related to this concept are a powerful guide for appropriate experimental designs (Noubactep and Caré, 2010a; 2010b; 2010c; Noubactep et al., 2009; Noubactep et al., 2010; Noubactep, 2011; Noubactep and Caré, 2011). On the other hand, regarding Fe<sup>0</sup> beds as 'Fe<sup>0</sup> amended sand filters' suggests that population balance models that account for pore and particle size distributions along with pore space topology (e.g. Bedrikovetsky, 2008) describe processes in dynamic Fe<sup>0</sup>/H<sub>2</sub>O systems with better accuracy than currently-used models (Jeen et al. 2011).

#### **Concluding remarks**

The use of Fe<sup>0</sup> for water treatment was based on the thermodynamically valid argument that Fe<sup>0</sup> is a relative strong reducing agent ( $E^0 = -0.44$  V/ESH). However, this assumption has overseen at least 2 important aspects of aqueous iron corrosion and their thermodynamics: solubility of iron hydroxides; and adhesion of oxide scale on metal (Noubactep, 2010a; 2010b). In fact, whether contaminant reduction by Fe<sup>0</sup> (direct reduction) occurs and contributes significantly to the process of contaminant removal remains unclear. However, it is certain that several groups of contaminants are quantitatively removed in Fe<sup>0</sup>/H<sub>2</sub>O systems and that these contaminants are adsorbed and co-precipitated (Noubactep, 2009d; Ghauch et al., 2010a; 2010b). Adsorbed and co-precipitated contaminants could be further reduced by electrons from Fe<sup>0</sup> (direct reduction), but more likely by electrons from Fe<sup>II</sup> or H/H<sub>2</sub> (indirect reduction). Additionally, some contaminants could be oxidised in the systems by in-situ generated Fenton-like reagents (Ghauch et al., 2010b). It is the aim of this communication to propose the substitution of the reductive transformation concept by that of adsorption/co-precipitation (and adsorptive size-exclusion).

It has been argued that 'no paradigm passes painlessly' (Heaney, 2003). The scientific objectivity should dictate the fate of any scientific concept regardless of its age or what has been invested in it. In the author's opinion, the proposed paradigm shift does not represent a danger for any industry but rather a chance for more systematic system designs. For example, the elimination of the constraint that contaminants should be reduced implies that surrogate parameters (e.g. dissolved organic carbon – DOC) can be used to monitor effluents for organics from treatment systems until breakthrough occurs. Afterwards, more precise analytic tools are needed to identify escaped organic species. On the other hand, the proposed new paradigm has enabled a better bed design and clarified the controversial issue of using inert admixture in Fe<sup>0</sup> beds (Noubactep et al., 2010). Furthermore, the new paradigm is about to revive Fe<sup>0</sup> household filters, e.g. the 3-Kolshi filters (Khan et al., 2000; Hussam and Munir, 2007; Hussam, 2009). The 3-Kolshi filters have been abandoned because of poor design, as recently demonstrated (Noubactep et al., 2010). The 3-Kolshi filters were replaced by very sustainable filters (SONO filters) in which iron shavings/filings were substituted by a porous Fe<sup>0</sup>-based composite (Hussam and Munir, 2007; Hussam, 2009).

The adsorption/co-precipitation concept has demonstrated that reduction is less important for the process of contaminant removal than had previously been assumed (O'Hannesin and Gillham, 1998; Gillham, 2010). Because contaminants are progressively enmeshed in the matrix of iron corrosion products, they are even more stable than if they were simply reduced or degraded. Accordingly, the proposed paradigm even sustains the acceptance of the Fe<sup>0</sup> technology. Researchers are given more possibilities for rational and systematic investigations of contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O systems as they can pay less relative attention to contaminant speciation. It is hoped that this opportunity will be used for a rapid development of the Fe<sup>0</sup> technology and its extension to other applications, as recently suggested by Antia (2010).

In conclusion, enhanced collaboration between experimental and modelling scientists is needed in order to expedite resolution of the key gaps in the understanding of the operation of processes governing the functionality of Fe<sup>0</sup> filtration systems. This closed collaboration is essential to frame new Fe<sup>0</sup> bed models.

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