On the validity of specific rate constants (k_{SA}) in Fe⁰/H₂O systems

C. Noubactep*

Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D-37077 Göttingen, Germany

ABSTRACT

The validity of the specific reaction rate constants (k_{SA}) in modelling contaminant removal in Fe⁰/H₂O systems is questioned. It is shown that the current k_{SA}-model does not consider the large reactive surface area provided by the in-situ formed oxide film, and thus the adsorptive interactions between contaminants and film materials. Furthermore, neither the dynamic nature of film formation nor the fact that the Fe⁰ surface is shielded by the film is considered. Suggestions are made how the k_{SA}-model could be further developed to meet its original goal.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Johnson et al. [1] performed an analysis of factors affecting the degradation rates of halogenated hydrocarbons by elemental iron (e.g. in Fe⁰/H₂O systems) with the aim to enable direct comparison between data from independent sources. Their results showed that first-order rate constants (k_{obs}) from both batch and column studies vary widely and without meaningful correlation. However, normalization of k_{obs} to iron surface area concentration yields a specific rate constant (k_{SA}) that varies by only one order of magnitude for individual contaminants. Since then, k_{SA} has been considered a practical descriptor of contaminant removal kinetics in Fe⁰/H₂O systems [2–4]. The validity of the k_{SA}-model was not established as suggested by the repeatedly reported non-linear relationship between k_{SA} and the Fe⁰ loading [2,5]. This note discusses the validity of the k_{SA}-model in light of recent reports on the mechanism of contaminant removal in Fe⁰/H₂O systems [6,7].

2. The k_{SA} model: surface area-normalized kinetics

For the sake of clarity the k_{SA}-model proposed by Johnson et al. [1] is given. In removal experiments by Fe⁰, the contaminant disappearance from the aqueous phase proceeds by kinetics that are first-order with respect to contaminant concentration. Therefore, first-order rate constants (k_{obs}) should be characteristic of a partic-

ular contaminant and set of conditions irrespective of contaminant concentration. Half-lives ($t_{1/2}$) derived from k_{obs} values should offer similar advantages of generality. Thus, k_{obs} and $t_{1/2}$ are used to characterize the kinetics of contaminant removal in Fe⁰/H₂O systems. Unfortunately, k_{obs} (or $t_{1/2}$) can not enable satisfactorily comparison of available data. Because the rate of contaminant reduction by Fe⁰ appeared also to be first-order with respect to the available reaction sites on Fe⁰ (available surface area), Johnson et al. [1] introduced k_{SA} as a more general descriptor of Fe⁰ reactivity. Therefore, k_{SA} has been reported to be more appropriate for remediation design calculations and other intersystem comparisons than k_{obs} (or $t_{1/2}$). The relation between k_{obs} and k_{SA} is given as:

$$k_{obs} = k_{SA}\rho_a \quad \text{and} \quad \rho_a = a_s\rho_m \tag{1}$$

where k_{SA} is the specific reaction rate constant ($L\,h^{-1}\,m^{-2}$), a_s is the specific surface area of Fe⁰ ($m^2\,g^{-1}$), ρ_m is the Fe⁰ mass loading ($g\,L^{-1}$), ρ_a is the surface area concentration of Fe⁰ ($m^2\,L^{-1}$).

The k_{SA}-model intrinsically suggests that straight-line plots should be obtained from k_{obs} versus ρ_a, a_s, or ρ_m (Eq. (1)). However, linear relationships of this sort have not been observed as a rule [1,2,5,8], suggesting that the validity of the model should be evaluated.

3. Discussion

While using the k_{SA} model, researchers have faced several difficulties demonstrating that k_{SA} might be a "strong but incomplete predictor of the reaction rate constants" [5]. The major reason for this situation has been identified as the interplay of different

* Tel.: +49 551 39 3191; fax: +49 551 399379.
E-mail address: cnoubac@gwdg.de.

processes (e.g., adsorption, electron transfer from a Fe^0 surface, Fe^0 surface passivation). Although adsorption was enumerated among the reasons for failure of the k_{SA}-model, little was done to correlate the relative affinities of individual contaminants to the iron corrosion products (oxide-film). The current discussion is based on the premise that contaminants are mostly reductively transformed by electrons from Fe^0 (direct reduction). However, the validity of this concept has been questioned [6,7]. The concept has been revisited and modified to a more accurate one (the adsorption/co-precipitation concept). The new concept stipulates that the fundamental contaminant removal mechanisms in Fe^0/H_2O systems are adsorption onto corrosion products and co-precipitation with corrosion products [6]. The major feature of the new concept relevant for the discussion in this note is that the Fe^0 is permanently covered by an oxide film. Therefore, for a contaminant molecule to reach the assumed reacting surface (e.g. Fe^0), it must migrate across a porous film of oxides. Moreover, contaminant can be retained in the film without reduction and redox reactions within the oxide film are partly stronger than those expected at the Fe^0 surface [6,7]. In other words a contaminant that has disappeared from the aqueous phase might be adsorbed onto or co-precipitated within the oxide film on Fe^0. Additionally, contaminants might be reduced by H/H_2 or Fe^{II} within the oxide film, more or less far from the Fe^0 surface. Irrespective of the nature of the oxide-film (porosity, thickness, electronic and ionic conductivity) the abundance of iron oxides as generated by mixing operations (i) diminish the accessibility of the Fe^0 surface and (ii) compete with the Fe^0 surface for contaminant removal as will be illustrated below. The first operation to lower these interactions is two minimize the abundance of iron oxides by avoiding (i) too large Fe^0 mass loadings, and (ii) too large mixing intensities.

4. Importance of iron corrosion products in Fe^0/H_2O systems

In discussing the removal process of redox-sensitive contaminants by Fe^0, iron corrosion products have been considered as surface coatings on Fe^0, mostly influencing the transfer of electrons from the underlying reductant [9]. In some cases iron corrosion was successfully used as generator of iron oxides for contaminant removal [10–12]. Nevertheless, the concept of contaminant reduction by Fe^0 (direct reduction) persists in the current literature. The importance of corrosion products in term of available surface area is illustrated here.

Consider a removal experiment occurring in 20 mL of a model solution with 0.1 g of a Fe^0 material (mass loading: $5 g L^{-1}$; iron content: 92%) having a specific surface area of $0.5 m^2 g^{-1}$ (surface loading: $2.5 m^2 L^{-1}$). The average particle size of the Fe^0 is 1.5 mm. The progression of the reaction can be recorded as the fraction of reacted Fe^0. For example, when 50% of the initial Fe^0 has reacted, the average particle size of the Fe^0 is 0.75 mm (one half of 1.5 mm). The surface of Fe^0 at that time can be deduced using Eq. (3) derived from Eq. (2) [13]:

$$S = \frac{6}{\rho d} \qquad (2)$$

$$\frac{S_2}{S_1} = \frac{d_1}{d_2} \qquad (3)$$

where ρ is the Fe^0 density ($7800 kg/m^{-3}$) [13].

On the other hand, while assuming for simplification that Fe_3O_4 is the sole generated iron oxide, the evolution of the relative surface area of Fe^0 and Fe_3O_4 are compared in Fig. 1. For comparison the evolution of the surface area of an inert material (granular activated carbon – GAC) is presented.
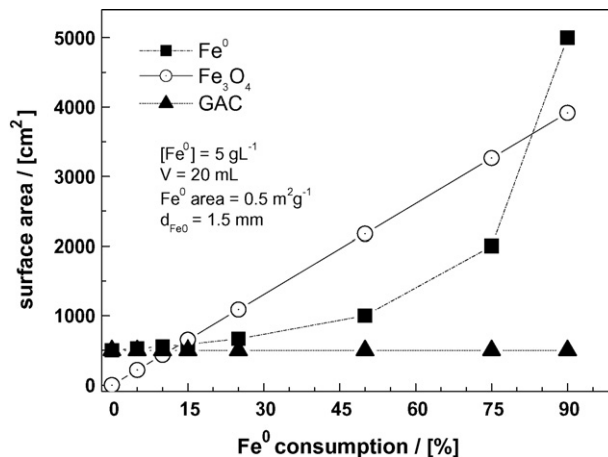

Fig. 1. Relative evolution of the surface area provided by elemental iron (Fe^0) and its corrosion products (e.g. Fe_3O_4) in a batch system. Granular activated carbon (GAC) is presented as an inert material whose surface area remains constant during the whole experiment. Crystalline Fe_3O_4 is taken as the model corrosion product; its specific area ($5.6 m^2 g^{-1}$) is taken from Farrell et al. [14]. The lines are not fitted functions, they simply connected points to facilitate visualization.

Fig. 1 shows the agreement of the theory that the Fe^0 surface area increases with decreasing particle size [13]. The surface area of granular activated carbon remains constant through the whole experiment and the surface area of Fe_3O_4, which is zero at the start of the experiments, increases linearly through the end of the experiment. Under the experimental conditions Fe_3O_4 provides more surface area to contaminants than Fe^0 when Fe^0 consumption is higher than 15%. Material consumptions larger than 50% are not likely to occur in laboratory batch experiments. When further considering the facts that (i) Fe_3O_4 is a layer on Fe^0 (physical barrier), and (ii) Fe_3O_4 interacts with contaminants, it is rather surprising that only the surface of Fe^0 has been considered in designing the k_{SA}-model.

In the reported simulations, the value of $5.6 m^2 g^{-1}$ for crystalline Fe_3O_4 reported by Farrell et al. [14] is used. However, crystalline Fe_3O_4 is generated by different steps from voluminous $Fe(OH)_2$ and $Fe(OH)_3$ through amorphous Fe_3O_4. In the course of these transformations (precipitation and recrystallization), contaminants are entrapped. This discussion considers neither the nature nor the concentration of these contaminants. The k_{SA}-model account neither for co-precipitated contaminants nor for contaminants adsorbed within the oxide film. This fraction has certainly disappeared from the aqueous solution and is considered reduced by the k_{SA}-model. Therefore, it is fair to say that the validity of the k_{SA}-model has not been examined by any scientific method.

5. Factors effecting k_{SA}

Despite surface area normalization, about one order of magnitude variability in contaminant disappearance rates were observed by Johnson et al. [1] and could not be satisfactorily explained. According to the authors, some of the variability could be due to differences in available surface area (Fe^0 pre-treatment, Fe^0 grain size distribution). A more profound source of variability in k_{SA} is believed to be due to the abundance of "non-reactive" fraction of total surface area as measured by the BET technique. "Reactive surface" is operationally defined as the fraction of surface area which contributes directly to contaminant reduction.

As discussed above, the Fe^0 surface is not directly accessible. Therefore, the kinetics of contaminant disappearance from the

aqueous solution is directly related to the abundance of corrosion products in the system. That is from the intrinsic reactivity of used Fe^0 and the operational conditions, mainly initial pH (and buffer application), Fe^0 mass loading, Fe^0 particle sizes, and mixing intensity. Since these parameters are interdependent the validity of the k_{SA} model should have been verified by performing parallel experiments (i) with different contaminants and the same Fe^0 materials under various conditions and (ii) with one contaminant and different Fe^0 samples under various conditions. On the basis of results from such experiments, an accurate discussion on the validity of the k_{SA}-model could be conducted. This ambitious task requires expertise beyond one or few research groups. Such an effort may provide the environmental science community with basic information for a non-site-specific iron wall design. Alternatively and complementarily, new routes are to be explored to better characterize the reactivity of Fe^0/H_2O systems.

6. Concluding remarks

The validity of the k_{SA}-model is dependent not only on the intrinsic Fe^0 reactivity and Fe^0 pre-treatment, but also on the operational experimental conditions (used Fe^0 mass loading, mixing intensity, Fe^0 particle size, initial pH value). Currently used experimental conditions are too different from each other for a useful comparison by means of the k_{SA}-model. The idea behind the k_{SA}-model is that there may be common underlying mechanisms for reactions in Fe^0/H_2O systems that provide a confidence for a non-site-specific permeable reactive barrier design [4]. This logical idea may be realized by a modified model taking into account the dynamic nature of the formation of corrosion products and their action as physical barriers on Fe^0. The first step to this ambitious goal may be a standard laboratory protocol that will enable direct comparisons of generated data and ease prospective works. A more concerted research effort is needed here.

References

[1] T.L. Johnson, M.M. Scherer, P.G. Tratnyek, Kinetics of halogenated organic compound degradation by iron metal, Environ. Sci. Technol. 30 (1996) 2634–2640.
[2] D.M. Cwiertny, A.L. Roberts, On the nonlinear relationship between k_{obs} and reductant mass loading in iron batch systems, Environ. Sci. Technol. 39 (2005) 8948–8957.
[3] Y.H. Liou, S.-L. Lo, C.-J. Lin, W.H. Kuan, S.C. Weng, Effects of iron surface pretreatment on kinetics of aqueous nitrate reduction, J. Hazard. Mater. B126 (2005) 189–194.
[4] K.L. McGeough, R.M. Kalin, P. Myles, Carbon disulfide removal by zero valent iron, Environ. Sci. Technol. 41 (2007) 4607–4612.
[5] H. Song, E.R. Carraway, Reduction of chlorinated methanes by nano-sized zero-valent iron: kinetics, pathways, and effect of reaction conditions, Environ. Eng. Sci. 23 (2006) 272–284.
[6] C. Noubactep, Processes of contaminant removal in "Fe^0–H_2O" systems revisited. The importance of co-precipitation, Open Environ. J. 1 (2007) 9–13.
[7] C. Noubactep, A critical review on the mechanism of contaminant removal in Fe^0–H_2O systems, Environ. Technol. 29 (2008) 909–920.
[8] H. Song, E.R. Carraway, Reduction of chlorinated ethanes by nanosized zero-valent iron: kinetics, pathways and effects of reaction conditions, Environ. Sci. Technol. 39 (2005) 6237–6245.
[9] M.M. Scherer, S. Richter, R.L. Valentine, P.J.J. Alvarez, Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean up, Rev. Environ. Sci. Technol. 30 (2000) 363–411.
[10] K. Karschunke, M. Gorny, M. Jekel, Arsenic removal by corrosion-induced adsorption, Vom Wasser 95 (2000) 215–222.
[11] T. Ludwig, M. Jekel, Copper and zinc removal from roof runoff in a iron-corrosion system, vom Wasser 107 (2007) 15–19 (in German).
[12] R. Rangsivek, M.R. Jekel, Removal of dissolved metals by zero-valent iron (ZVI): kinetics, equilibria, processes and implications for stormwater runoff treatment, Water Res. 39 (2005) 4153–4163.
[13] C. Macé, S. Desrocher, F. Gheorghiu, A. Kane, M. Pupeza, M. Cernik, P. Kvapil, R. Venkatakrishnan, W.-X. Zhang, Nanotechnology and groundwater remediation: a step forward in technology understanding, Remed. J. 16 (2006) 23–33.
[14] J. Farrell, W.D. Bostick, R.J. Jarabeck, J.N. Fiedor, Uranium removal from ground water using zero valent iron media, Ground Water 34 (1999) 618–624.