1 **On the Validity of Specific Rate Constants (k_{SA}) in Fe^0/H$_2$O Systems**

2   Noubactep C.

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

4   e-mail: cnoubac@gwdg.de; Tel. +49 551 39 3191, Fax: +49 551 399379

5

6   **Abstract**

7   The validity of the specific reaction rate constants (k_{SA}) in modelling contaminant removal in

8   Fe^0/H$_2$O systems is questioned. It is shown that the current k_{SA}-model does not consider the

9   large reactive surface area provided by the in-situ formed oxide film, and thus the adsorptive

10 interactions between contaminants and film materials. Furthermore, neither the dynamic

11 nature of film formation nor the fact that Fe^0 surface is shielded by the film is considered.

12 Suggestions are made how the k_{SA}-model could be further developed to possibly meet its

13 original goal.

14 **Keywords:** Adsorption; Co-precipitation, Rate constants; Reduction; Zerovalent iron.

15 **Introduction**

16 Johnson et al. [1] performed an analysis of factors effecting the degradation rates of

17 halogenated hydrocarbons by elemental iron (e.g. in Fe^0/H$_2$O systems) with the aim to enable

18 direct comparisons between data from independent sources. Their results showed that first-

19 order rate constants (k_{obs}) from both batch and column studies vary widely and without

20 meaningful correlation. However, normalization of k_{obs} to iron surface area concentration

21 yields a specific rate constant (k_{SA}) that varies by only one order of magnitude for individual

22 contaminants. Since then, k_{SA} has been considered a practical descriptor of contaminant

23 removal kinetics in Fe^0/H$_2$O systems [2-4]. The validity of the k_{SA}-model was not established

24 as suggested by the repeatedly reported non-linear relationship between k_{SA} and the Fe^0

25 loading [2,5]. This note discusses the validity of the k_{SA}-model on the light of recent reports

26 on the mechanism of contaminant removal in Fe^0/H$_2$O systems [6,7].

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 Fe^0, 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 particular 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 characterise the kinetics of contaminant removal in Fe^0/H_2O systems. Unfortunately, k_{obs} (or $t_{1/2}$) could not enable satisfactorily comparison of available data. Because the rate of contaminant reduction by Fe^0 appeared also to be first order with respect to the available reaction sites on Fe^0 (available surface area), Johnson et al. [1] introduced k_{SA} as a more general descriptor of Fe^0 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:

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

where k_{SA} is the specific reaction rate constant ($Lh^{-1}m^{-2}$), a_s is the specific surface area of Fe^0 ($m^2 g^{-1}$), ρ_m is the Fe^0 mass loading (gL^{-1}), ρ_a is the surface area concentration of Fe^0 (m^2L^{-1}). The k_{SA}-model intrinsically suggests that straight-line plots should be obtained from k_{obs} versus ρ_a, as, 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 closely discussed.

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 processes (e.g., adsorption, electron transfer from an Fe^0 surface, Fe^0 surface passivation). Although adsorption was enumerated among the reasons of failure of the k_{SA} model, little was done to

53 correlate the relative affinities of individual contaminants to the iron corrosion products

54 (oxide-film). The current discussion is based on the premise that contaminants are mostly

55 reductively transformed by electrons from Fe^0 (direct reduction). However, the validity of this

56 concept has been questioned [6,7]. The concept has been revisited and completed to a more

57 accurate one (the adsorption/co-precipitation concept). The new concept stipulates that the

58 fundamental contaminant removal mechanisms in Fe^0/H_2O systems are adsorption onto

59 corrosion products and co-precipitation with corrosion products [6]. The major feature of the

60 new concept relevant for the discussion in this note is that the Fe^0 is permanently covered by

61 an oxide film. Therefore, for a contaminant molecule to reach the assumed reacting surface

62 (e.g. Fe^0), it must migrate across a porous film of oxides. Moreover, contaminant can be

63 retained in the film without reduction and redox reaction within the oxide film are partly

64 stronger than those expected at the Fe^0 surface [6,7]. In other words a contaminant that has

65 disappeared from the aqueous phase might be adsorbed onto or have co-precipitated within

66 the oxide film on Fe^0. Additionally, contaminant might be reduced by H/H_2 or Fe^{II} within the

67 oxide film, more or less far from the Fe^0 surface. Irrespective from the nature of the oxide-

68 film (porosity, thickness, electronic and ionic conductivity) the abundance of iron oxides as

69 generated by mixing operations (i) diminishes the accessibility of the Fe^0 surface and (ii)

70 competes with the Fe^0 surface for contaminant removal as will be illustrated below. The first

71 operation to lower these interactions is two minimize the abundance of iron oxides by

72 avoiding (i) too large Fe^0 mass loadings, and (ii) too large mixing intensities.

73 **Importance of iron corrosion products in Fe^0/H_2O systems**

74 In discussing the removal process of redox-sensitive contaminants by Fe^0, iron corrosion

75 products have been considered as surface coatings on Fe^0, mostly influencing the transfer of

76 electrons from the underlying reductant [9]. In some cases iron corrosion was successfully

77 used as generator of iron oxides for contaminant removal [10-12]. Nevertheless, the concept

78   of contaminant reduction by Fe^0 (direct reduction) persists in current literature. The

79   importance of corrosion products in term of available surface area is illustrated here.

80   Let's consider a removal experiment occurring in 20 mL of a model solution with 0.1 g of a

81   Fe^0 material (mass loading: 5 gL^{-1} – iron content: 92 %) having a specific surface area of 0.5

82   m^2g^{-1} (surface loading: 2,5 m^2L^{-1}). The average particle size of the Fe^0 is 1.5 mm. The

83   progression of the reaction can be recorded as the fraction of reacted Fe^0. For example, when

84   50 % of the initial Fe^0 has reacted, the average particle size of the Fe^0 is 0.75 mm (one half of

85   1.5 mm). The surface of Fe^0 at that time can be deduced using equation 3 derived from

86   equation 2 [13]:

87                  $$S = 6 / (\rho * d) \hspace{5cm} (2)$$

88                  $$S_2/S_1 = d_1/d_2 \hspace{5cm} (3)$$

89   Where ρ is the Fe^0 density (7,800 kg/m^3) [13].

90   On the other hand while supposing for simplification that Fe_3O_4 is the sole generated iron

91   oxide, the evolution of the relative surface area of Fe^0 and Fe_3O_4 are compared in figure 1. For

92   comparison the evolution of the surface area of an inert material (granular activated carbon -

93   GAC) is presented.

94   Figure 1 shows the agreement of the theory that the Fe^0 surface area increases with decreasing

95   particle size [13]. The surface area of granular activated carbon remains constant through the

96   whole experiment and the surface area of Fe_3O_4, which is zero at the start of the experiments,

97   increases linearly through the end of the experiment. Under the experimental conditions

98   Fe_3O_4 provides more surface area to contaminants than Fe^0 when Fe^0 consumption is higher

99   than 15 %. Material consumptions larger than 50 % are not likely to occur in laboratory batch

100 experiments. When further considering the facts, that (i) Fe_3O_4 is a layer on Fe^0 (physical

101 barrier), and (ii) Fe_3O_4 interacts with contaminants, it is rather surprising that only the surface

102 of Fe^0 has been considered in designing the k_{SA}-model.

103   In the reported simulations, the value of 5.6 m^2g^{-1} for crystalline Fe_3O_4 reported by Farrell et

104   al. [14] is used. However, crystalline Fe_3O_4 is generated by different steps from voluminous

105     $Fe(OH)_2$ and $Fe(OH)_3$ through amorphous Fe_3O_4. In the course of these transformations

106   (precipitation and recrystallization), contaminants are entrapped. This discussion considers

107   neither the nature nor the concentration of the contaminant. The k_{SA}-model does not account

108   for co-precipitated contaminants nor for contaminants adsorbed within the oxide film. This

109   fraction has certainly disappeared from the aqueous solution and is considered reduced by the

110   k_{SA}-model. Therefore, it is fair to say that the validity of the k_{SA}-model has not been examined

111   by any scientific method.

112   **Factors Effecting k_{SA}**

113   Despite surface area normalization, about one order of magnitude variability in contaminant

114   disappearance rates was observed by Johnson et al. [1] and could not be satisfactorily

115   explained. According to the authors, some of the variability could be due to differences in

116   available surface area (Fe^0 pre-treatment, Fe^0 grain size distribution). A more profound source

117   of variability in k_{SA} is believed to be due to the abundance of "non reactive" fraction at total

118   surface area as measured by the BET technique. "Reactive surface" is operationally defined as

119   the fraction of surface area, which contributes directly to contaminant reduction.

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

121   contaminant disappearance from the aqueous solution is directly related to the abundance of

122   corrosion products in the system. That is from the intrinsic reactivity of used Fe^0 and the

123   operational conditions, mainly initial pH (and buffer application), Fe^0 mass loading, Fe^0

124   particle sizes, mixing intensity. Since these parameters are interdependent the validity of the

125   k_{SA} model should have been verified by performing parallel experiments (i) with different

126   contaminants and the same Fe^0 materials under various conditions and (ii) with one

127   contaminant and different Fe^0 samples under various conditions. On the basis of results from

128   such experiments, an accurate discussion on the validity of the k_{SA} model could be conducted.

129 This ambitious task requires expertise beyond one or few research groups. Such an effort may

130 provide the environmental science community with basic information for a non-site-specific

131 iron wall design. Alternatively or complementarily, new routes are to be explored to better

132 characterize the reactivity of Fe^0/H_2O systems.

Concluding Remarks

134 The validity of the k_{SA}-model is dependent, not only on the intrinsic Fe^0 reactivity and Fe^0

135 pre-treatment, but also on the operational experimental conditions (used Fe^0 mass loading,

136 mixing intensity, Fe^0 particle size, initial pH value). Currently used experimental conditions

137 are too different from each other for a purposeful comparison by means of the k_{SA}-model. The

138 idea behind the k_{SA}-model is that there may be common underlying mechanisms for reactions

139 in Fe^0/H_2O systems that provide a confidence for a non-site-specific permeable reactive

140 barrier design [4]. This logical idea may be materialized by a modified model taking into

141 account the dynamic nature of the formation of corrosion products and their action as physical

142 barriers on Fe^0. The first step to this ambitious goal may be a standard laboratory protocol that

143 will enable direct comparisons of generated data and ease prospective works. More research is

144 needed, more concerted research.

References

150 [1] T.L. Johnson, M.M. Scherer, P.G. Tratnyek, Kinetics of halogenated organic compound

151   degradation by iron metal. Environ. Sci. Technol. 30 (1996), 2634–2640.

152 [2] D.M. Cwiertny, A.L. Roberts, On the nonlinear relationship between k_{obs} and reductant

153   mass loading in iron batch systems. Environ. Sci. Technol. 39 (2005), 8948–8957.

154 [3] Y.H. Liou, S.-L. Lo, C.-J. Lin, W.H. Kuan, S.C. Weng, Effects of iron surface
155   pretreatment on kinetics of aqueous nitrate reduction. J. Hazard. Mater. B126 (2005),
156   189–194.

157 [4] K.L. McGeough, R.M. Kalin, P. Myles, Carbon disulfide removal by zero valent iron.
158   Environ. Sci. Technol. 41 (2007), 4607–4612.

159 [5] H. Song, E.R. Carraway, Reduction of chlorinated methanes by nano-sized zero-valent
160   iron. kinetics, pathways, and effect of reaction conditions. Environ. Eng. Sci. 23 (2006),
161   272–284.

162 [6] C. Noubactep, Processes of contaminant removal in "Fe^0–H_2O" systems revisited. The
163   importance of co-precipitation. Open Environ. J. 1 (2007), 9–13.

164 [7] C. Noubactep, A critical review on the mechanism of contaminant removal in Fe^0–H_2O
165   systems. Environ. Technol. 29 (2008), 909–920.

166 [8] H. Song, E.R. Carraway, Reduction of chlorinated ethanes by nanosized zero-valent iron:
167   kinetics, pathways and effects of reaction conditions. Environ. Sci. Technol. 39 (2005),
168   6237–6245.

169 [9] M.M. Scherer, S. Richter, R.L. Valentine, P.J.J. Alvarez, Chemistry and microbiology of
170   permeable reactive barriers for in situ groundwater clean up. Rev. Environ. Sci.
171   Technol. 30 (2000), 363–411.

172 [10] K. Karschunke, M. Gorny, M. Jekel, Arsenic removal by corrosion-induced adsorption.
173   Vom Wasser 95 (2000), 215–222.

174 [11] T. Ludwig, M. Jekel, Copper and zinc removal from roof runoff in a iron-corrosion
175   system (in German). vom Wasser 107 (2007), 15–19.

176 [12] R. Rangsivek, M.R. Jekel, Removal of dissolved metals by zero-valent iron (ZVI):
177   Kinetics, equilibria, processes and implications for stormwater runoff treatment. Water
178   Res. 39 (2005), 4153–4163.

179   [13] C. Macé, S. Desrocher, F. Gheorghiu, A. Kane, M. Pupeza, M. Cernik, P. Kvapil, R.

180   Venkatakrishnan, W.-X. Zhang, Nanotechnology and groundwater remediation: A step

181   forward in technology understanding. Remed. J. 16 (2006), 23–33.

182   [14] J. Farrell, W.D. Bostick, R.J. Jarabeck, J.N. Fiedor, Uranium removal froum ground

183   water using zero valent iron media. Ground Water 34 (1999), 618–624.

184   Figure 1

185

186
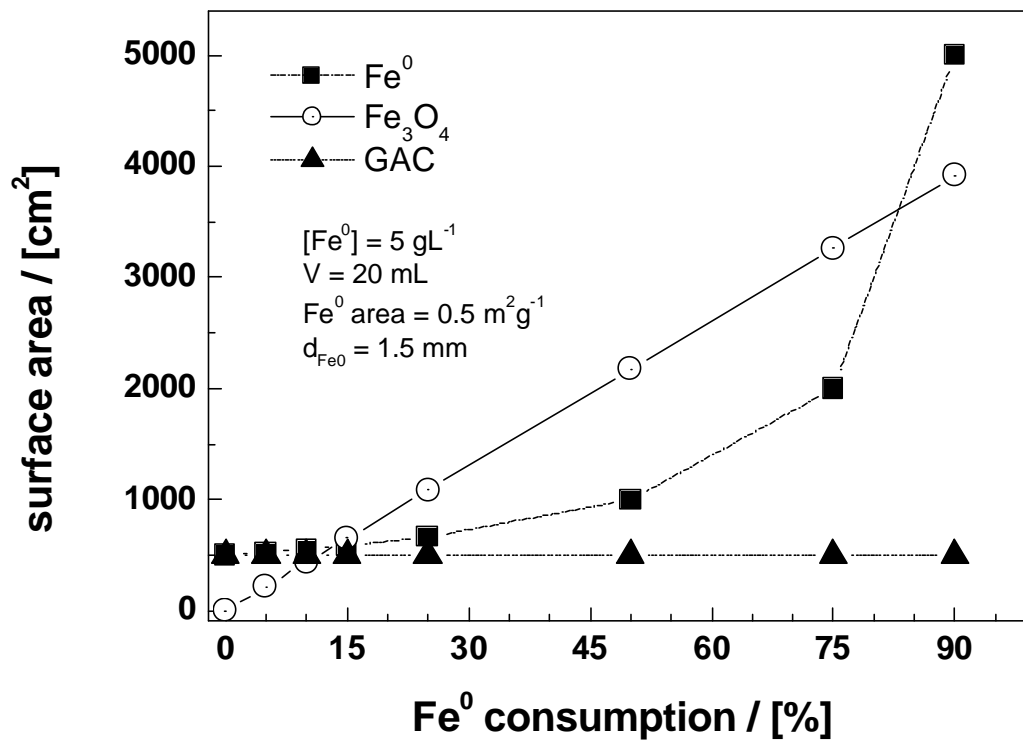
187 **Figure 1**: Relative evolution of the surface area provided by elemental iron (Fe^0) and its

188   corrosion products (e.g. Fe_3O_4) in a batch system. Granular activated carbon

189   (GAC) is presented as an inert material whose surface area remains constant

190   during the whole experiment. Crystalline Fe_3O_4 is taken as the model corrosion

191   product; its specific area (5.6 m^2g^{-1}) is taken from Farrell et al. [14]. The lines are

192   not fitted functions, they simply connected points to facilitate visualization.