

1 **Metallic Iron for Environmental Remediation: Learning from the *Becher***

2 ***Process***

3 Noubactep C.

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

5 Tel. +49 551 39 3191, Fax: +49 551 399379

6 e-mail: cnoubac@gwdg.de

7 **Abstract**

8 Metallic iron (Fe^0) is a moderately reducing agent that has been reported to be capable of
9 reducing many environmental contaminants. Reduction by Fe^0 used for environmental
10 remediation is a well-known process to organic chemists, corrosion scientists and
11 hydrometallurgists. However, considering Fe^0 as a reducing agent for contaminants has faced
12 considerable scepticism because of the universal role of oxide layers on Fe^0 in the process of
13 electron transfer at the $\text{Fe}^0/\text{oxide}/\text{water}$ interface. This communication shows how progress
14 achieved in developing the *Becher process* in hydrometallurgy could accelerate the
15 comprehension of processes in $\text{Fe}^0/\text{H}_2\text{O}$ systems for environmental remediation. The *Becher*
16 *process* is an industrial process for the manufacture of synthetic rutile (TiO_2) by selectively
17 removing metallic iron (Fe^0) from reduced ilmenite (RI). This process involves an aqueous
18 oxygen leaching step at near neutral pH. Oxygen leaching suffers from serious limitations
19 imposed by limited mass transport rates of dissolved oxygen across the matrix of iron oxides
20 from initial Fe^0 oxidation. In a $\text{Fe}^0/\text{H}_2\text{O}$ system pre-formed oxide layers similarly act as
21 physical barrier limiting the transport of dissolved species (including contaminants and O_2) to
22 the $\text{Fe}^0/\text{H}_2\text{O}$ interface. Instead of this universal role of oxide layers on Fe^0 , improper
23 conceptual models have been developed to rationalize electron transfer mechanisms at the
24 $\text{Fe}^0/\text{oxide}/\text{water}$ interface.

25 **Keywords:** *Becher process*, Leaching, Oxide layers, Remediation, Zerovalent Iron.

26 **Capsule:** Results from *Becher process* are valuable for mass transfer in $\text{Fe}^0/\text{H}_2\text{O}$ systems.

27 **Introduction**

28 Permeable reactive barriers of elemental iron (Fe^0 walls or remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems) are
29 a valuable technological application that has been shown to be both environmentally friendly
30 and cost-effective in the removal of various substances from contaminated waters [1-7]. Since
31 its development in 1990 by Canadian hydrogeologists numerous papers have been written on
32 the topic and approximately 120 iron walls installed worldwide [4]. Even though the
33 importance of the mechanism of contaminant removal was recognised in the early stage of
34 technology development [1,8], there is still discussion about the mechanism of contaminant
35 removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems [9-12]. The main reason cited for reported discrepancies was the
36 improper consideration of the significance of the oxide-film on the process of contaminant
37 removal [11,12]. In fact, after considerable initial scepticism [2], it was accepted that
38 contaminants are removed in $\text{Fe}^0/\text{H}_2\text{O}$ systems by an abiotic reductive transformation. Based
39 on this consensus, “the role of oxides in reduction reactions” were discussed [13].
40 Accordingly, the oxide layers may act either as: (i) a semiconductor to relay electron transfer
41 from Fe^0 to the contaminants (direct reduction) or (ii) Fe^{II} adsorbent to yield very reactive
42 adsorbed Fe^{II} (so-called structural Fe^{II} for indirect reduction). Additionally, electron transfer
43 from the Fe^0 body exposed by pitting of the oxide layer to contaminants is likely to occur. The
44 objective of this paper is to show how the consideration of progress achieved in developing
45 the *Becher process* in the hydrometallurgy, could accelerate the comprehension of processes
46 in Fe^0 walls by carefully surveying the impact of the oxide-layer on contaminant mass transfer
47 to the $\text{Fe}^0/\text{H}_2\text{O}$ interface. For the sake of clarity the *Becher process* is presented first.

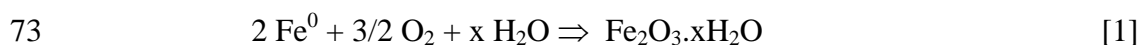
48 **The *Becher process***

49 The *Becher process* is an environmentally friendly, cost-effective extraction method for
50 upgrading ilmenite from 55 % TiO_2 to about 94 % TiO_2 by reduction with charcoal [14-22]. A
51 typical feed made up of 55 % ilmenite (FeTiO_3), 38 % pseudorutile ($\text{Fe}_2\text{Ti}_3\text{O}_9$) and 7 % rutile
52 (TiO_2) is heated in air at about 1000 °C to oxidise the Fe^{II} in the ilmenite to Fe^{III} resulting in a

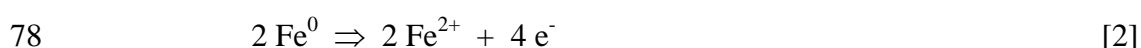
53 phase known as pseudobrookite ($\text{Fe}_2\text{TiO}_5 = \text{Fe}_2\text{O}_3 + \text{TiO}_2$). Pseudobrookite is then reduced
 54 with coal (C/CO) in an iron reduction kiln at 1100 °C. This carbothermic reaction reduces the
 55 iron in the pseudobrookite to the metallic (Fe^0). The reduction product (reduced rutile - RI)
 56 consists mainly of grains of Fe^0 embedded in a matrix of titanium dioxide [19,22]. After
 57 cooling RI (approximately $2 \text{ Fe} + \text{TiO}_2$), embedded Fe^0 should be leached from (or “rusted
 58 out” of) the matrix (about 58 % Fe) at near neutral pH. Leaching Fe^0 from RI is achieved by
 59 oxidation with dissolved oxygen from air (so-called “aerial oxidation”) mostly with
 60 ammonium chloride (NH_4Cl) acting as a catalyst for rusting. Since the solution is not
 61 buffered, the pH will rise resulting in the formation of various iron oxides. Magnetite (Fe_3O_4)
 62 is the preferred product since it can be magnetically separated from TiO_2 . Ideally, RI should
 63 be upgraded by dissolved O_2 in the presence of NH_4Cl from 42 % to approximately 94 %
 64 TiO_2 . However, the oxygen leaching of Fe^0 suffers from a serious limitations imposed by the
 65 sluggish mass transport rates of low soluble oxygen ($\leq 8 \text{ mg/L}$) to the interface $\text{Fe}^0/\text{H}_2\text{O}$. This
 66 physical barrier of iron corrosion products (oxide-layer or oxide-film) characterizes the
 67 similarity between the leaching process in the *Becher process* and contaminant removal in
 68 $\text{Fe}^0/\text{H}_2\text{O}$ systems.

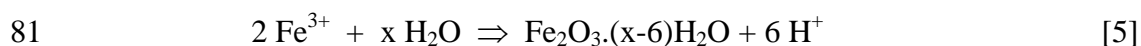
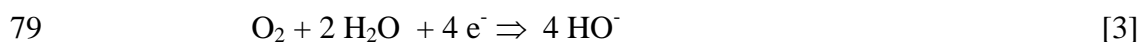
69 **Mechanism of iron removal in the *Becher process***

70 Aqueous iron oxidation (corrosion) by dissolved oxygen (O_2) has been extensively described
 71 in the literature, including the aeration step in the *Becher process* for the manufacture of
 72 synthetic rutile [14,15,18,19,22]. The overall reaction can be represented as:



74 The primary process is essentially an electrochemical reaction made up of (i) an anodic Fe^0
 75 oxidation (Eq. 2), and a cathodic O_2 reduction (Eq. 3). Fe^{2+} ions from Eq. 2 are (at least
 76 partially) further oxidized by dissolved O_2 to Fe^{3+} ions (Eq. 4), which are subsequently
 77 hydrolysed and precipitated as $\text{Fe}_2\text{O}_3 \cdot (x-6)\text{H}_2\text{O}$ (Eq. 5).





82 It was established that the iron oxide products varied with time, yielding an iron oxide
83 mixture of unknown composition (FeOOH, Fe₂O₃, Fe₃O₄) [15,17].

84 A survey of the reactions above reveals three major features: (i) dissolved oxygen is
85 consumed by both heterogeneous (electrochemical Fe⁰ dissolution) and homogenous (Fe²⁺
86 oxidation) reactions; (ii) additional solid phases are formed (FeOOH, Fe₂O₃, Fe₃O₄) during
87 the process leading to a “three”-phase (Fe⁰-oxides-H₂O) reaction system; (iii) in-situ formed
88 solid phases influence the rates of O₂ mass transfer to the Fe⁰ surface. Clearly, iron oxides as
89 inert solid phase influence O₂ mass transfer and thus the kinetics of heterogeneous reactions at
90 the interface Fe⁰/H₂O. The impact of iron oxide will increase with increasing reaction time
91 since the amount of oxides is increasing. Accordingly, the heterogeneous reactions at the Fe⁰
92 surface can be divided into two phases: (i) an initial constant rate phase, followed by (ii) a
93 second phase, in which a steep decrease in rate is expected and was observed [15].

94 ***Becher process versus contaminant removal in Fe⁰/H₂O systems***

95 In the *Becher process* iron removal from a matrix of reduced ilmenite (RI - 58 % Fe⁰ and 42
96 % TiO₂) by oxidation with dissolved O₂ is the goal. The oxidation is performed in the
97 presence of NH₄Cl to limit iron oxide precipitation in the vicinity of RI (see below).
98 Nevertheless, iron oxides precipitate and the goal of a matrix with 94 % TiO₂ is sometimes
99 difficult to achieve [19,22]. Generated iron oxides are regarded as inert micro-particles
100 influencing mass transfer between RI and dissolved O₂. To accelerate mass transfer and thus
101 maximize O₂ leaching in the *Becher process*, RI might be ground to small particle sizes
102 and/or intensive solution mixing (stirring, agitating) yielding particle suspension might be
103 applied.

104 In permeable reactive barriers, an elemental iron material (usually > 80 % Fe) is used; Fe⁰
105 oxidation is ideally induced by the oxidized form of a contaminant. No external addition of
106 chemical to limit iron oxide precipitation is suitable. The aquifer might contain chloride ions
107 (Cl⁻) known for their destabilizing effects on the formation of oxide layers on Fe⁰. With
108 regards to the objective (contaminant removal), Fe⁰ oxidation by dissolved O₂ should be
109 considered a disturbing factor yielding iron oxides that should act as physical barrier for
110 contaminant transport to the Fe⁰/H₂O interface (as in the *Becher process*). This is the
111 fundamental role of an oxide-layer (oxide-film), which should have been considered as the
112 rule. The exceptions of conducting oxide-layers or lattice Fe^{II} surface sites [13,23,24] could
113 be treated separately. This has not been the case, showing that lessons from the *Becher*
114 *process* are very helpful for the development of the Fe⁰ technology. Contrary to the *Becher*
115 *process*, acceleration of mass transfer of contaminant to the Fe⁰/H₂O interface should be
116 limited to conditions of mass-transfer control [11,12]. Under these conditions material
117 suspension should not occur and the formation of the oxide layer on Fe⁰ should not be
118 significantly disturbed.

119 The most important features common to the *Becher process* and contaminant removal in
120 remediation Fe⁰/H₂O systems are: (i) iron dissolution and iron precipitation yielding a
121 complex oxide mixture of unknown composition, (ii) Fe⁰ and Fe^{II} are potential reducing
122 agents, and (iii) the weight fraction of iron oxide particles would increase from zero at the
123 beginning to higher proportions depending on the reaction progress. The net result for both
124 processes is a multi-solid reaction system involving two types of solids of widely differing
125 size (RI/Fe⁰ and iron oxides). The large changes in the solid composition during the reaction
126 can be expected to influence the mass transfer of species to the Fe⁰/H₂O interface and thereby
127 play a significant role in the determination of reaction rates.

128 The major difference between both processes is that iron oxides can be regarded as inert in the
129 *Becher process* but are contaminant adsorbents in Fe⁰/H₂O systems. Furthermore, during their

130 polymerisation and precipitation, iron (hydr)oxides may sequester contaminants in their
131 matrix (so-called co-precipitation) [11,12]. Therefore, contaminants can be immobilized by
132 oxide-layers on Fe^0 regardless of any chemical or electrochemical redox reaction, possibly
133 involving Fe^0 . Finally, oxides in $\text{Fe}^0/\text{H}_2\text{O}$ systems are good adsorbents for Fe^{II} from Fe^0
134 oxidation yielding adsorbed Fe^{II} (structural Fe^{II}). Structural Fe^{II} is a very strong reducing
135 agent for inorganics and organics [25]. Table 1 summarises some relevant processes involved
136 in remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems and in the *Becher process*.

137 It should be acknowledged that increasing attention has been paid to the role of oxide layer on
138 Fe^0 in the mechanisms of contaminant reductive transformation in the literature
139 [8,10,13,24,26-29,35]. However, these experiments were mostly performed to gain
140 information on the nature of surface coatings and their influence on kinetics and reaction
141 pathways of the reductive transformation of water pollutants. While these experiments show
142 the role of oxide layers (iron oxides/hydroxides) on Fe^0 as possible electron mediators, the
143 *Becher process* indicates that oxide layers fundamentally act as physical barriers. Recent
144 works [11,12] demonstrated that contaminants are primarily removed by adsorption and co-
145 precipitation within the oxide layers and are stable as long as the iron oxide is not dissolved.

146 **Lessons from the *Becher process*:**

147 Modelling is now a fundamental step in science, since it allows a better understanding of
148 investigated systems. Modelling can be used to support experimental design, operation
149 control, experiment planning, experiment optimization, experiment scaling, and system or
150 results analysis [30]. Upon adequately representing a system, one might be able to scale-up,
151 design, optimize, or control a system. To be efficient, each model needs (i) relevant
152 parameters, (ii) relevant data, and (iii) expertise of the modeller in terms of adequate
153 computational methods. Models for the adequate understanding of remediation $\text{Fe}^0/\text{H}_2\text{O}$
154 systems could benefit from expertise from the *Becher process* if they considered the above-
155 mentioned differences (see also table 1). In particular, the interplay between mass transfer and

156 kinetics encountered in the *Becher process* will help to better plan experiments as well as
157 improve the interpretation of results from extensive studies on the kinetics of contaminant
158 removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems. Similar to the *Becher process*, this involves both Fe^0 and Fe^{II}
159 oxidation by relevant dissolved species (including contaminants and oxygen).

160 Several different types of models have been developed with regards to the *Becher process*
161 [17,18]. These models consider various aspects of the operation such as O_2 mass transfer and
162 the presence of solid, liquid and gaseous phases. For example, the model developed by
163 Geetha and Surender [18] considered the *Becher process* as a multi-phase system involving a
164 complex interplay between mass transfer and chemical reactions. This model can be further
165 developed to meet the specifics of remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems. In particular the following
166 aspects need to be considered: (i) the fact that iron dissolution should be coupled to
167 contaminant removal, (ii) the limited availability of oxygen, which is a disturbing factor
168 (concurrent for Fe^0 oxidation), (iii) the fact that iron oxides are not inert particles on mass
169 transfer rates but effective contaminant removing agents (adsorption and co-precipitation),
170 and (iv) the specific interactions of individual contaminants with the oxide layer on Fe^0 . It can
171 be emphasized that the overall process of contaminant removal under field conditions will be
172 controlled by an internal diffusion through the oxide layer, since almost all contaminants are
173 larger in size than molecular oxygen (the oxidant of the *Becher process*).

174 Another important result from the *Becher process* is highlighted by the work of Farrow et al.
175 [21] who compared the role of sodium chloride (NaCl) and ammonium chloride (NH_4Cl) on
176 the process of selective iron leaching. It is well-known that the chloride ion plays an
177 important role in the breakdown of oxide layers and is therefore a desirable constituent in any
178 electrolyte solution used for the promotion of iron corrosion [31,32]. To elucidate the role of
179 ammonium ions in the leaching reaction, parallel experiments with 0.1 M of each chloride
180 were carried out at 70°C . In both cases the dissolved iron concentration and the bulk solution
181 pH were monitored during the course of the reaction. The results showed that the ammonium

182 chloride plays three distinct and important roles in the selective leaching [21]: (i) NH_4^+ acts as
183 a buffer for hydroxyl ions (OH^-) and prevents excessively high local pH values, which might
184 otherwise cause precipitation of iron (II) hydroxide before the iron (II) ions could diffuse
185 from the rutile matrix; (ii) the ammonia (NH_3) formed as a result of this buffering reaction
186 complexes iron (II) ions until they also have moved away from the regions of high pH, thus
187 preventing the precipitation of iron (II) hydroxide in the pores of the rutile; (iii) the chloride
188 ion helps to break down any passive films which might form during aeration. The large
189 difference in the leaching rates for NaCl and NH_4Cl could be explained using pH data, which
190 indicate that most of the reactions in NH_4Cl takes place at a pH of about 4, and most of the
191 reactions in NaCl takes place at a pH between 9 and 10. These results show clearly that in
192 investigating process relevant for remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems while avoiding iron oxide
193 precipitation, it will be more advantageous to work with NH_4Cl than with strong chelating
194 agents like ethylenediaminetetraacetic acid [1,33] of larger molecular size and little buffering
195 capacity.

196 A further relevant result from the *Becher process* is obtained by Bruckard et al. [22] on the
197 optimisation of selective iron leaching using the anthraquinone-based redox catalysts while
198 guaranteeing the formation of the preferred magnetite as the reaction product. This result
199 could be very important for enhancing long-term reactivity of $\text{Fe}^0/\text{H}_2\text{O}$ systems. The redox
200 catalysts are effective for three main reasons [22, 34]: (i) their electrochemical reactions are
201 fast and reversible, (ii) their redox potentials are located between those of the $\text{Fe}^{\text{II}}/\text{Fe}^0$ and
202 $\text{H}_2\text{O}/\text{O}_2$ couples such that their oxidised forms (the anthraquinones) oxidise metallic iron and
203 their reduced forms (the semi-quinones or hydroquinones) are oxidised by oxygen, and (iii)
204 both the reduced and oxidised forms of the catalysts are stable in solution. A modest
205 enhancement of contaminant reduction by Fe^0 in the presence of several quinonoid model
206 compounds (e.g. juglone, lawsone, and anthraquinone disulfonate) was also reported by
207 Tratneyk et al. [24,35] in remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems. However, the observed effects were

208 not expected to be significant in field applications. Yet, if quinonoid model compounds
209 effectively favour the formation of electronic conductive magnetite (Fe_3O_4) as reported by
210 Bruckard et al. [22], their effects for long-term reactivity of Fe^0 walls should be significant.
211 More research under conditions pertinent to remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems is needed to clarify
212 this issue.

213 **Concluding remarks**

214 While the complexity of mass-transfer in remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems is yet to be properly
215 assessed, the *Becher process* for the manufacture of synthetic rutile has already dealt with the
216 prediction of solid-liquid mass transfer in systems in which particles of various densities and
217 sizes are available [15,17-19]. The results achieved in developing the *Becher process* could be
218 very useful to investigations regarding processes in Fe^0 walls. In particular, the interplay
219 between mass transfer and kinetics reported in the *Becher process* could help in improving the
220 interpretation of data from extensive investigations on the kinetics of contaminant removal in
221 $\text{Fe}^0/\text{H}_2\text{O}$ systems. For this purpose, specifics of the $\text{Fe}^0/\text{H}_2\text{O}$ system (limited O_2 availability,
222 reactivity of the oxide layer, dynamic nature of the film formation and transformation) should
223 to be properly considered and data should be obtained under relevant experimental conditions
224 [11,12]. Furthermore, electron mediators have been unambiguously described in the *Becher*
225 *process* [22]. Electron mediators facilitate electron transport from Fe^0 to reducible species
226 (oxygen, contaminants), they can undergo many successive reduction/oxidation cycles in the
227 process and act as catalysts. Catalytic effects of quinonoid model compounds in remediation
228 $\text{Fe}^0/\text{H}_2\text{O}$ systems should be further investigated.

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323 **Table 1:** Overview of some relevant processes involved in remediation Fe⁰/H₂O systems and
 324 in the *Becher Process*. In both cases the anodic reaction is the electrochemical dissolution of
 325 Fe⁰ which is followed by the chemical precipitation of Fe^{II}/Fe^{III} oxyhydroxides (oxide layer).
 326 Irrespective of the cathodic reactants (O₂, contaminants), the rate of aqueous iron corrosion is
 327 proportional to the total amount of reducible species transferred to the Fe⁰ surface. In the
 328 *Becher Process*, enhanced O₂ mass-transfer rate can be achieved by various mixing operations
 329 and the extent of Fe⁰ dissolution increased for example by using ammonium chloride. In
 330 groundwater remediation species transport to Fe⁰ depends on natural hydrodynamic
 331 conditions.

Process	Groundwater treatment	Becher process
Objective	Contaminant removal	Upgrading of reduced ilmenite (42 % TiO ₂) to synthetic rutile (94 % TiO ₂)
Used material	Fe-based material (up to 99.0 % Fe)	Reduced ilmenite (approx. 58 % Fe)
Method	Oxidation of Fe ⁰ by contaminants	Selective oxidation of Fe ⁰ by O ₂
Role of Fe^{II}	suitable contaminant reducing agent within the oxide layer	O ₂ scavenger within the oxide layer (non-relevant process – side reaction)
Nature	Environmental process (controlled exclusively by environmental conditions)	Industrial process (O ₂ leaching process can be intensified e.g., by the use of ferrous chloride)
Conditions	6.0 < pH < 9.5 Temperature lower than 20 °C limited O ₂ availability (< 2 mg/L) no iron oxyhydroxides at t = 0 various iron oxyhydroxides at t > 0	pH > 6.0 Temperature: ambient to 130 °C O ₂ available (ideally 8 mg/L) no iron oxyhydroxides at t = 0 various iron oxyhydroxides at t > 0
Limitations (passivation)	Fe-oxides limit mass transport rates of species (incl. O ₂) to the Fe ⁰	Fe-oxides limit mass transport rates of oxygen to the Fe ⁰ surface
Remedy to passivation	Use of bimetallics and nanoparticles. Use of ultrasound.	use of ammonium chloride as a buffering and complexing agent (initial pH = 4.5)

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