

1 **Elemental metals for environmental remediation: Learning from cementation process**

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5

6 **Abstract**

7 The further development of Fe⁰-based remediation technology depends on the profound
8 understanding of the mechanisms involved in the process of aqueous contaminant removal.
9 The view that adsorption and co-precipitation are the fundamental contaminant removal
10 mechanisms is currently facing a harsh scepticism. Results from electrochemical cementation
11 are used to bring new insights in the process of contaminant removal in Fe⁰/H₂O systems. The
12 common feature of hydrometallurgical cementation and metal-based remediation is the
13 heterogeneous nature of the processes which inevitably occurs in the presence of a surface
14 scale. The major difference between both process is that the surface of remediation metals is
15 covered by layers of own oxide(s) while the surface of the reducing metal is covered by
16 porous layers of the cemented metal. The porous cemented metal is necessarily electronic
17 conductive and favours further dissolution of the reducing metal. For the remediation metal,
18 neither a porous layer nor a conductive layer could be warrant. Therefore, the continuation of
19 the remediation process depends on the long-term porosity of oxide scales on the metal
20 surfaces. These considerations rationalized the superiority of Fe⁰ as remediation agent
21 compared to thermodynamically more favourable Al⁰ and Zn⁰. The validity of the
22 adsorption/co-precipitation concept is corroborated.

23 **Key words:** Adsorption; Cementation, Co-precipitation; Surface scale; Zerovalent Iron.

24 **Capsule:** Hydrometallurgy teaches that sustaining oxide scale formation and transformation
25 on Fe⁰ is the best way to warrant long service life of iron walls.

26

26 **1 Introduction**

27 The use of metallic iron (Fe^0) for environmental remediation is now well established [1-4].
28 However, the exact mechanism of aqueous contaminant removal in the presence of Fe^0 is not
29 fully understood. It is univocally accepted that contaminant removal is due to the process of
30 iron oxidative dissolution (iron corrosion). However, a net discrepancy exists on the role of
31 the oxide scale on Fe^0 in the process of contaminant removal. Oxide scale formation on Fe^0 at
32 $\text{pH} > 4.5$ is a fundamental characteristic of aqueous iron corrosion [5-8]. The universal oxide
33 scale on Fe^0 is either regarded as beneficial (blessing) or inhibitory (curse) for aqueous
34 contaminant removal in the presence of Fe^0 .

35 The prevailing concept was introduced in the early phase of investigations regarding the
36 mechanism of aqueous contaminant removal by Fe^0 [9,10]. This concept considers that
37 contaminant is removed mainly by an heterogeneous chemical reduction, ideally at the surface
38 of Fe^0 . Accordingly, the oxide scale on Fe^0 is a curse as its represents a diffusion barrier
39 slowing down the kinetics of contaminant removal [11,12]. The initial model assuming the
40 local existence of oxide-free Fe^0 in the aqueous solution was proven unrealistic by Bonin et
41 al. [13]. A new conceptual model for the reductive transformation was proposed [13,14]. The
42 conceptual model of Bonin et al. [13] indicated that the reductive transformation is controlled
43 by electron transfer through the surface film. Accordingly the film must be electronic
44 conductive. However, no such conductive film is expected in nature [6,15,16]. Moreover, the
45 concept regarding oxide-scale as curse is built on the premise that Fe^0 is a strong reducing
46 agent. The concept is strictly applicable only to reducible contaminants.

47 It is important to notice that the reductive transformation concept has never been univocally
48 accepted [17,18]. For example, Warren et al. [18] wrote that “a convincing mechanism for the
49 reductive dehalogenation of haloorganics by zero-valence metals has not yet been proposed.
50 Matheson and Tratnyek [9] maintained that dehalogenation was not mediated by $\text{H}_2(\text{g})$ or
51 $\text{Fe}(\text{II})$ in the bulk aqueous-phase solution, suggesting that observed reactions take place at the

52 metal surface.” Three years later, O'Hannesin and Gillham [1] acknowledged that “there is a
53 broad consensus that the process is an abiotic redox reaction involving reduction of the
54 organic compound and oxidation of the metal”. Despite this “broad consensus”, the reductive
55 transformation concept has felt to explain many experimental observations [19-21].

56 An alternative concept regards the oxide scale on Fe^0 as beneficial (a blessing) for the process
57 of aqueous contaminant removal [22-25]. Independent researchers could traceably
58 demonstrate that quantitative contaminant removal is only observed when iron corrosion
59 products are allowed to precipitate in the system [26-31]. Their results suggest that adsorption
60 and co-precipitation are the fundamental (not the dominant or the major) contaminant removal
61 mechanisms. Accordingly, relevant contaminants could be further (quantitatively) chemically
62 transformed (reduced or oxidized). The first merit of this concept it that its explains why a
63 contaminant like zinc which is non reducible by Fe^0 (Tab. 1) could be quantitatively removed
64 in the presence of Fe^0 [32].

65 The present communication is motivated by recent publications speaking disparagingly about
66 the concept of adsorption/co-precipitation as fundamental mechanisms of aqueous
67 contaminant removal in the presence of Fe^0 [33,34]. The similarities between aqueous
68 contaminant removal by Fe^0 and metal iron cementation on elemental metals (mostly Al^0 , Fe^0 ,
69 Zn^0) will be discussed with the aim to present results from the hydrometallurgical process of
70 cementation which could help to understand and further develop the process of aqueous
71 contaminant removal by Fe^0 . Both processes are heterogeneous and the metal surface is
72 covered by a scale acting as diffusion barrier. For the sake of clarity the diffusion barrier in
73 the Fe^0 remediation will first be presented.

74 **2 Aqueous contaminant removal by metallic iron**

75 Aqueous iron corrosion on which remediation with metallic iron is based is an heterogeneous
76 electrochemical process. A simplistic mechanism for iron oxidative dissolution involves four
77 major steps: (i) diffusion of the oxidizing agent (H^+ , O_2 , contaminant) to the Fe^0 surface, (ii)

78 adsorption of the oxidizing agent onto the iron surface, (iii) the reduction of the oxidizing
79 agent, and (iv) diffusion of reaction products (including Fe^{II} species) away from the reactive
80 site on Fe^0 . Because aqueous iron corrosion (at $\text{pH} > 4.5$) is always coupled to the formation
81 of an oxide scale on the Fe^0 surface, the rate of the oxidizing agent diffusion to the iron
82 surface is necessarily the limiting step for the corrosion process which is said to be “diffusion
83 controlled” [7,16]. If, the rate of iron corrosion were limited by the adsorption or electron
84 transfer steps, the reaction would be said to be “chemical controlled”, “surface controlled”, or
85 “reaction controlled” (reaction-limited).

86 The presentation above recalled, that iron corrosion at $\text{pH} > 4.5$ is a “diffusion controlled” or
87 mass transfer limited process. Accordingly, there should have been no need to discuss the
88 active form of rate control in the process of contaminant removal in the presence of metallic
89 iron under subsurface conditions. Clearly, attempts to determine whether the process of
90 contaminant removal in the presence of Fe^0 in a field reactive wall is mass transfer or
91 reaction-limited [9,17,35] was not necessary as this was well-documented before the event of
92 the iron remediation technology [25].

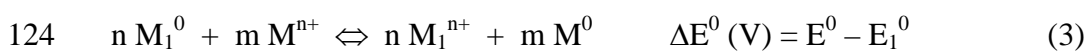
93 In batch experiments or fluidised beds, the rate of contaminant removal by Fe^0 could be
94 increased by increasing the mass transfer using various mixing operations (e.g. agitation,
95 stirring, vibration) [36,37]. However, one should acknowledge that such mixing operations
96 are not applicable to packed beds and field reactive walls [25,36,38]. As discussed in details
97 elsewhere [25], the use of various mixing systems with the resulting mixing intensities and
98 their impact on the process of contaminant removal in the presence of Fe^0 is the main reason
99 why the inconsistent concept of reductive transformation has survived for more than a decade.
100 The example of the usefulness of mixing operations in investigating processes involving iron
101 corrosion reveals that care must be taken while using well-documented results from other
102 branches of science in designing experiments and/or interpreting new experimental data. A
103 further example is the way to experimentally evidence a chemically controlled reaction. To

104 demonstrate the occurrence of a chemical reaction in a system, the temperature of the system
 105 should be varied. An increased reaction rate with increasing temperature is a strong proof for
 106 chemical reaction [39]. However, increased contaminant removal with increasing temperature
 107 is not necessarily coupled to contaminant reduction by Fe^0 as water is also an oxidizing agent
 108 and resulting corrosion products are contaminant scavengers. In other words, contaminant
 109 removal might only indirectly be coupled to proven chemical reactions.

110 The present communication aims at presenting some aspects of the electrochemical
 111 cementation process as used in the hydrometallurgy and discuss their usefulness for metallic
 112 iron as currently used in environmental remediation. Two particular aspects will be discussed
 113 in some details: (i) the differential reactivity and the suitability of aluminium, iron and zinc as
 114 removing agent, and (ii) the proper consideration of the surface scale on Fe^0 . For the sake of
 115 clarity the process of cementation will be first presented.

116 **3 Cementation and its use in the hydrometallurgy**

117 Cementation is an electrochemical process by which a more noble metal ion (M^{n+} - Eq. 1) is
 118 precipitated from solution and replaced by a metal higher in the electromotive series (M_1^{m+} -
 119 Eq. 2) [39-45]. Cementation, also known as contact reduction or metal displacement, is
 120 necessarily a spontaneous heterogeneous reaction ($\Delta G^0 < 0$) that takes place through the
 121 galvanic cell $M_1^0/M_1^{m+} // M^{n+}/M$ (Eq. 3).



126 $z = n.m$ is the number of electrons exchanged between M_1 and M and F the Faraday's
 127 constant.

128 The thermodynamic basis of cementation can be summarized as follows: The standard free
 129 energy (ΔG^0 - Eq. 4) of the cementation process after Eq. 3 must be negative (spontaneous

130 reaction). This requires that ΔE^0 is positive or $E_1^0 < E^0$. In other words, cementation consists
131 in the spontaneous heterogeneous reduction of a metallic ion present in solution (M^{n+}) by a
132 more electropositive sacrificial metal (M_1^0). M_1 is the metal higher in the electromotive series
133 (Table 1). It is evident from table 1 that, from a pure thermodynamic perspective, Al should
134 be the most powerful metal for cementation followed by Zn and Fe. However as will be
135 discussed later the stability of the oxide scale on the individual metals is determinant for the
136 progress of their oxidative dissolution.

137 Cementation is one of the most effective and economic techniques for removing valuable
138 metals from industrial effluents [43,44,45,47,48]. The technique is affordable because of its
139 relative simplicity, ease of control, and low energy consumption. A cementation reaction is an
140 heterogeneous processes limited by diffusion through the mass transfer boundary layer.
141 However, unlike many other heterogeneous reaction systems, cementation reactions are
142 unique in that the reaction product usually does not impede the reaction progress but rather
143 frequently enhances the reaction kinetics ([49] and references therein). Discussing the
144 differential impact of diffusion layers on metals in cementation and contaminant removal is
145 the major reason for this communication and will be presented below. The major difference
146 between both processes relies in the intrinsic nature of each process. However both processes
147 are based on the same concept: The electrochemical reduction. Cementation is a technological
148 process for which the experimental conditions could be case specific optimised. Contaminant
149 removal should be operated on a case-specific basis without changing the chemistry of the
150 system. From this difference it arises that the pH value (and thus the nature of the surface
151 scale) and the mixing operation could be regarded as the two key factors for the design of
152 each system. The further presentation will be focussed on Al, Fe and Zn.

153 **4 Cementation using Al, Fe and Zn**

154 The control of the pH value is a key task for the cementation process for a variety of reasons
155 including: (i) corrosion damage of reactors, (ii) excess dissolution of the reducing metal (Al,

156 Fe and Zn), and (iii) hydroxide precipitation. Accordingly, the determination of the optimal
157 pH value is an important economical issue for any cementation plant. The impact of pH on
158 the performance of Al, Fe and Zn as reducing metal will be discussed on the basis of the
159 results from Hg^{2+} cementation by Al^0 , Fe^0 and Zn^0 [50]. The experiments were performed for
160 30 minutes in Erlenmeyer's, with an initial mercury concentration equal to 500 mg/L and
161 using 10 mol of reducing agent for each mol of mercury. The pH-dependent evolution of the
162 system was recorded (Fig. 1). Figure 1a represents the variation of final pH value as function
163 of the initial pH for three parallel experiments. Figure 1b represents the variation of the molar
164 ratio dissolved reducing metal to the cemented Hg as function of the initial pH. The
165 stoichiometric ratio is 1.00 for Zn and Fe and 0.67 for Al.

166 Figure 1a clearly shows that, pH stabilises at a constant value for Al (4.7) and Fe (3.7)
167 whereas the pH in the system with Zn was still varying (after 30 min). This behaviour is
168 strongly related to the amount of reducing metal dissolved. Accordingly the order of
169 increasing reactivity based on metal dissolution is: $\text{Fe} < \text{Al} < \text{Zn}$. Remember that the order of
170 increasing reactivity based on the electrode potential was: $\text{Fe} < \text{Zn} < \text{Al}$. The difference is
171 certainly due to the differential hydrolysis and solubility behaviour of resulted metallic ions
172 (Al^{3+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, Zn^{2+}) and the adherence of resulting metal oxides to basic surface. These
173 issues will not be discussed here. The most important feature from the pH-dependant
174 cementation is to find the optimal pH for the optimal yield which is ideally the pH where the
175 stoichiometry of the reaction approaches the theoretical value (0.67 for Al and 1.00 for Fe and
176 Zn).

177 Figure 1b shows that, the optimal pH regions are 5.0 - 6.0 for Al, 3.0 - 5.0 for Fe, and 4.0 -
178 7.0 for Zn. It should be further considered that as pH value increases the precipitation of metal
179 hydroxides is progressively significant. Metal hydroxides are known for their adsorptive
180 properties which are disturbing for the cementation process. Based on these considerations,

181 Anacleto and Carvalho [50] performed their Hg^{2+} cementation reaction under following
182 conditions: aluminium (3.0 - 4.0), iron (3.0), and zinc (4.0 - 6.0).

183 **4.1 Nature of the diffusion layer on reducing metals**

184 The presentation above clearly shows that cementation is optimally performed under
185 conditions where ions from the reducing metal (here, Al^{3+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, Zn^{2+}) are soluble and do
186 not readily hydrolyse and precipitate. The precipitating elemental metal (e.g. Hg^0) is
187 necessarily insoluble. Therefore, precipitating metals accumulate at the surface of the
188 reducing metal (Al^0 , Fe^0 or Zn^0). This metallic layer is porous, and dendritic and thus
189 significantly enhances kinetics of the reaction [41,49]. In essence, only a smooth, coherent
190 deposit can inhibit the cementation reaction. According to Power and Ritchie [40],
191 cementation reactions whose constituent half-reactions have electrode potentials which differ
192 by greater than 0.36 V are likely to be diffusion-controlled (Tab. 1). As recalled above the
193 diffusion is favoured by the porous nature of the metallic deposit which is additionally
194 electronic conductive and constitute a path for electron transport. In other words, the
195 cementation process continues despite the metallic scale for two main reasons: (i) metallic
196 ions are soluble and transported through the porous layer to the bulk solution, (ii) the metallic
197 layer (cemented deposit) is electronic conductive. Consequently, for contaminant reduction to
198 be quantitative in a $\text{Fe}^0/\text{H}_2\text{O}$ system, the oxide scale should be electronic conductive and
199 porous.

200 **5 Diffusion layers on remediation elemental metals**

201 Diffusion is a spontaneous process involving mobility of species due to the existence of a
202 concentration gradient in a system. The extend of diffusion depend on (i) the properties of the
203 diffusing species (including their size), and (ii) the structure of the diffusion layer
204 (connectivity, morphology, porosity, pore site distribution or tortuosity). Here the diffusion
205 layer is a precipitated scale (oxide scale).

206 Oxide layers on remediation metals are formed at $\text{pH} > 5.0$ which is the pH of natural waters
207 (assuming comparable redox potential). Upon immersion in an aqueous solution, any reactive
208 metal is instantaneously covered by an oxide scale [6]. The initial scale is possibly porous
209 (non-protective film) but may be more or less rapidly transformed to an impervious scale
210 (protective film). The porosity of the oxide scale is very determinant for the progress of metal
211 oxidative dissolution which is coupled to oxide scale formation and contaminant removal.
212 It is well-documented that upon immersion, the surface of aluminium is rapidly covered by a
213 very thin and adherent layer of oxide (protective layer). Accordingly, despite theoretical
214 thermodynamic suitability, Al is a worse remediation metal than Fe and Zn. As seen above
215 (Fig. 1a), Zn is the most efficient cementation agent because of its more rapid dissolution.
216 However, because Zn^{II} is the only soluble Zn species, the progress of the dissolution will
217 yield to a formation of a dense oxide film on Zn^0 which will progressively develop to an
218 impervious layer with the time. For Fe^0 , the existence of two soluble species (Fe^{II} and Fe^{III})
219 and several iron oxides with different crystal structures [24] is a guarantee for the long term
220 non-protectiveness. Accordingly, Fe^0 is best remediation agent. The non toxic nature of iron
221 species and the lost-cost of Fe^0 materials are further reasons for its intensive use as
222 remediation agent.

223 **6 Concluding remarks**

224 The formation of surface scale on immersed elemental metals is a common feature for
225 remediation with metallic elements and electrochemical cementation (Tab. 2). In both cases
226 the surface scale primarily inhibits the metal dissolution and thus the kinetics of the concerned
227 process. The formation of an oxide film on the cementation agent can be prevented (or
228 limited) by a rational selection of the operational conditions (e.g. pH value, amount of
229 cementation agent, and mixing operations). Provided these operational conditions are
230 accurately selected, the cementation process should not be essentially inhibited by the metal
231 deposit which is even beneficial in some cases [43,45,50].

232 The avoidance of the oxide scale formation on elemental metals under natural conditions is
233 not possible. Therefore, one could only discuss or access their porosity and their electronic
234 conductivity. As a rule an electronic conductive oxide scale can not be expected under
235 environmental conditions. In fact, regardless from the availability and abundance of
236 molecular oxygen (anoxic or oxic conditions), Fe^0 is always covered by a multi-layer of oxide
237 and hydroxide mixture of which only magnetite (Fe_3O_4) and unstable forms (FeO , green rusts)
238 are electronic conductive. Consequently, the reactivity of Fe^0 for environmental remediation
239 is mostly due to the porosity of the oxide scale and factors influencing its evolution (e.g. pH
240 value, water salinity, nature of contaminants). To sustain Fe^0 reactivity under environmental
241 conditions, appropriate reactive materials should be selected or manufactured. In this regard,
242 porous composites like those used in SONO arsenic filters could be used [51,52].

243 In conclusion, a careful consideration of the optimal conditions for the hydrometallurgical
244 process of cementation using Al^0 , Fe^0 , and Zn^0 has enabled the precision of the role of oxide
245 scale in the process of contaminant removal with the same metals. Its appears that considering
246 the oxide scale as a curse for the remediation process was a mistake. The oxide scale is rather
247 beneficial for the process of contaminant removal by Fe^0 . Moreover, removed contaminants
248 and their potential reaction products are progressively enmeshed in the matrix of ageing
249 corrosion products and are very stable under natural conditions. Accordingly, instead of
250 maintaining an inconsistent concept [33,34,53,54], the scientific community should focus his
251 attention on ways to sustain the corrosion process rather to try to free the Fe^0 from
252 spontaneously generated corrosion products. It should be observed that operational tools
253 presently used to sustain Fe^0 reactivity such as: (i) using smaller particle size of Fe^0 (including
254 nano-scale Fe^0), (ii) mixing experimental systems or (iii) using bimetallic systems all result in
255 increased corrosion products generation. Accordingly, all these tools corroborate the
256 adsorption/co-precipitation concept.

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- 389

389 **Table 1:** Standard electrode potential of selected metals relevant for hydrometallurgical
390 cementation. Electrode potentials are arranged in increasing order of E^0 . An
391 electrochemical reaction occurs between an oxidant of higher E^0 and a reducing
392 agent of lower E^0 . In other words, a more noble metal ion is precipitated from
393 solution and replaced in solution by a metal higher in the electromotive series. It is
394 clear that the three most powerful reducing agents are Al, Zn and Fe. E^0 values are
395 from ref. [46].
396

Electrode	Reaction	E^0 (V)	Eq.
Al ³⁺ /Al	Al ³⁺ + 3 e ⁻ ⇌ Al ⁰	-1.660	(5)
Zn ²⁺ /Zn	Zn ²⁺ + 2 e ⁻ ⇌ Zn ⁰	-0.763	(6)
Fe ²⁺ /Fe	Fe ²⁺ + 2 e ⁻ ⇌ Fe ⁰	-0.440	(7)
Cd ²⁺ /Cd	Cd ²⁺ + 2 e ⁻ ⇌ Cd ⁰	-0.403	(8)
Ni ²⁺ /Ni	Ni ²⁺ + 2 e ⁻ ⇌ Ni ⁰	-0.250	(9)
Pb ²⁺ /Pb	Pb ²⁺ + 2 e ⁻ ⇌ Pb ⁰	-0.126	(10)
H ⁺ /H ₂	2 H ⁺ + 2 e ⁻ ⇌ H ₂	0.000	(11)
Cu ²⁺ /Cu	Cu ²⁺ + 2 e ⁻ ⇌ Cu ⁰	0.337	(12)
Cu ⁺ /Cu	Cu ⁺ + e ⁻ ⇌ Cu ⁰	0.521	(13)
Pb ⁴⁺ /Pb	Pb ⁴⁺ + 4 e ⁻ ⇌ Pb ⁰	0.700	(14)
Hg ₂ ²⁺ /Hg	Hg ₂ ²⁺ + 2 e ⁻ ⇌ 2 Hg ⁰	0.789	(15)
Ag ⁺ /Ag	Ag ⁺ + e ⁻ ⇌ Ag ⁰	0.799	(16)
Hg ²⁺ /Hg	Hg ²⁺ + 2 e ⁻ ⇌ Hg ⁰	0.854	(17)
Au ³⁺ /Au	Au ³⁺ + 3 e ⁻ ⇌ Au ⁰	1.290	(18)

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398

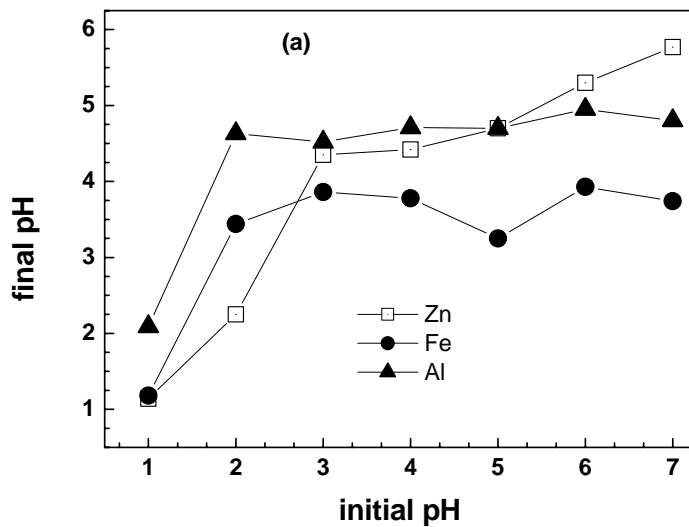
398 **Table 2:** Characteristic features of the electrochemical processes of cementation and metal-
 399 based remediation. The processes further differ by the fate of the surface scale.
 400 While cemented metal deposits are recovered, metal oxides are responsible for
 401 contaminant removal but also for porosity loss.
 402

Process	Objective	pH	Surface scale		
			nature	porosity	conductivity
Cementation	Metal recovery	< 5.0	Metal	high	high
Remediation	Decontamination	> 6.0	Metal oxide	variable	low

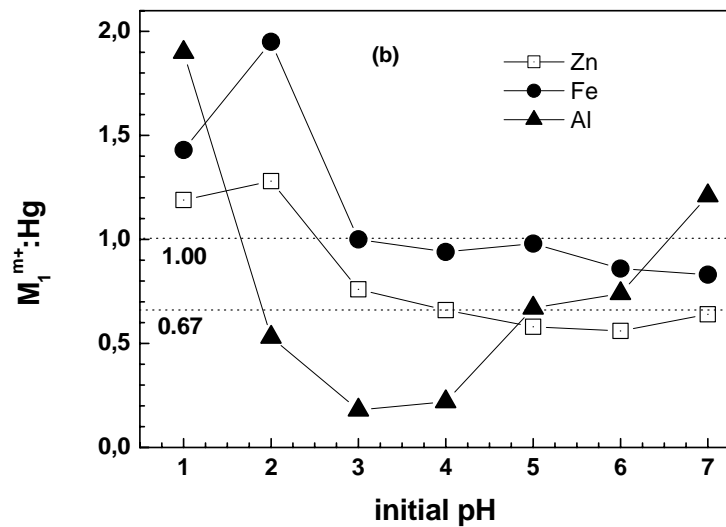
403
 404
 405

405 **Figure 1**

406



407



408

409

410 **Figure 1:** Final pH value (a) and molar ratio dissolved metal to cemented Hg (b) with

411 different initial pH values. The lines are not fitting functions, they simply connect

412 points to facilitate visualization. Data from ref. [50].