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# Magnetic-field-assisted electrodeposition of metal to obtain conically structured ferromagnetic layers

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## Abstract

Micro- or nano-structured ferromagnetic layers often possess superior electrocatalytic properties but are difficult to manufacture in general. The present work investigates how a magnetic field can possibly support local cone growth on a planar electrode during electrodeposition, thus simplifying fabrication. Analytical and numerical studies were performed on conical structures of mm size to elaborate the influence of the magnetic forces caused by an electrode-normal external field. It is shown that, beside the Lorentz force studied earlier in the case of single cones [1], the magnetic gradient force enabled by the field alteration near the ferromagnetic cathode significantly supports cone growth. Detailed studies performed for sharp and flat single cones allow conclusions to be drawn on the support at different stages in the evolution of conical deformations. Furthermore, the influence from neighboring cones is studied with arrays of cones at varying distances apart. Nearby neighbors generally tend to mitigate the flow driven by the magnetic forces. Here, the support for cone growth originating from the magnetic gradient force is less heavily affected than that from the Lorentz force. Our results clearly show that the magnetic field has a beneficial effect on the growth of ferromagnetic conical structures, which could also be useful on the micro- and nanometer scales.

*Keywords:*

metal electrodeposition, magnetic field, surface-structured electrode, Lorentz force, magnetic gradient force, numerical simulation

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## 1. Introduction

Conical micro- and nano-structures have numerous applications due to their particular physical and chemical properties which appear when length scales are reduced. Inspired by cicada wings, super-hydrophobic surfaces covered with arrays of conical protuberances were reported to have good self-cleaning properties [2, 3]. For electrochemical applications, nano-structured electrodes are of great importance due to their enhanced catalytic activity. Great efforts have been devoted to increasing the activity of noble-metal-free catalysts by surface nano-structuring in order to replace the rare, expensive Pt-based catalysts widely used in fuel cell technologies [4, 5, 6]. In this respect, conically structured ferromagnetic electrodes have also been reported to reduce the overpotential for the hydrogen evolution reaction by enhancing the active surface area and supporting the bubble detachment [7, 8].

Among the various methods of synthesizing arrays of micro- and nano-cones, electrochemical deposition techniques have been widely applied [9, 10, 11]. As the current density can be expected to be greater at cathode regions closer to the counter-electrode, according to Faraday's law, the deposition rate is higher at e.g. the tip of a cone compared to other flat electrode regions [12]. This mechanism generally supports the growth of non-uniformities during template-free deposition. In order to further enhance a possible structuring effect during deposition, magnetic fields may be utilized. In the past, magnetic fields have already proven a promising tool for controlling the mass transport of the ionic species during electrodeposition processes. A variety of effects can be achieved, among them the enhancement of the limiting current [13, 14, 15, 16], the homogenization of the deposit thickness [17, 18], the modification of the morphology of the deposited layers [19, 20, 21], the reduction of dendrite growth in Li metal batteries [22, 23], and the enhancement of hydrogen evolution in electrolysis [24, 25, 26, 27]. Structured deposits down to the micrometer scale were obtained using planar but magnetically patterned electrodes. Due to the strongly inhomogeneous magnetic field created locally, a correspondingly patterned deposit follows [28, 29]. However, the local modification of the magnetic field during growth of a ferromagnetic elevation has not yet been investigated in detail, which adds motivation for the present study.

It is well known that applying a magnetic field during electrodeposition causes magnetic forces to act on the electrolyte and to drive a flow. These forces are the Lorentz force [13, 30, 31], and possibly also the magnetic gradient force [32, 33, 34]. If the magnetic forces can be designed such as to generate an electrolyte flow which brings fresh electrolyte towards the tip of a cone, local mass transfer would be enhanced and, thus, cone growth would be supported. For the Lorentz force generated by a surface-normally oriented magnetic field, this beneficial effect has firstly been shown near single copper cones [1]. Here, simulations and measurements based on shadowgraphy and Mach-Zehnder interferometry were performed, and a

41 moderate effect could be observed in a weak magnetic field of 60 mT. The Lorentz  
 42 force is given by the vector product of the current density  $\mathbf{j}$  and the magnetic flux  
 43 density  $\mathbf{B}$ ,

$$\mathbf{f}_L = \mathbf{j} \times \mathbf{B} \quad (1)$$

44 Here, as the electrolyte velocity is usually low ( $U \ll 1\text{m/s}$ ), flow-induced parts of  
 45 the current density and the magnetic field may safely be neglected [35]. Figure 1(a)  
 46 schematically shows the flow near a conical cathode driven by the Lorentz force  $\mathbf{f}_L$   
 47 originating from an external magnetic field directed vertically upwards ( $\mathbf{B}_0$ ). For  
 48 diamagnetic and paramagnetic media, there is  $\mathbf{B} \approx \mathbf{B}_0$ . Then, the vertical magnetic  
 49 field and the radial component of the current density caused by the electric field lines  
 50 bending near the cone surface create an azimuthal flow around the cone [1]. The  
 51 centrifugal acceleration of the electrolyte away from the cone caused by this primary  
 52 rotating flow then gives rise to a secondary downward flow which brings fresh bulk  
 electrolyte to the cone tip and enriches the boundary layer [33].

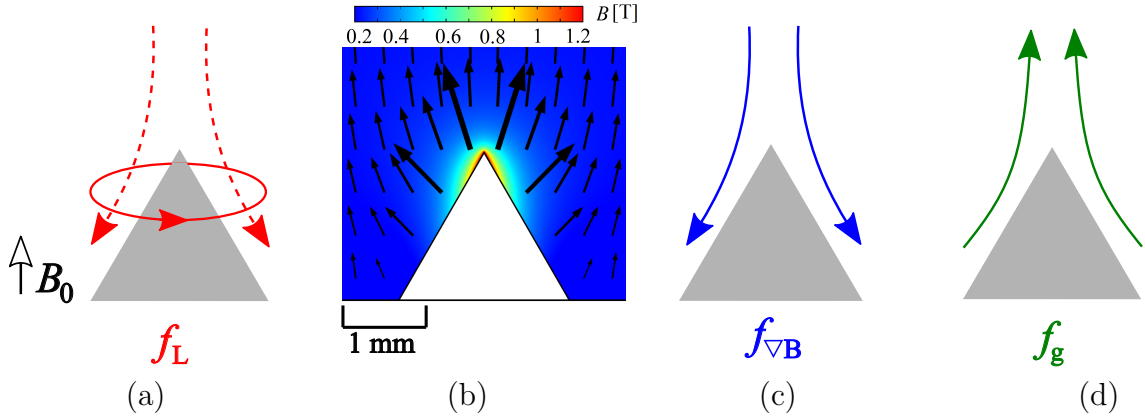


Figure 1: Sketch of the flows generated by (a) the Lorentz force  $\mathbf{f}_L$  (primary and secondary flow indicated by solid and dashed lines, respectively), (c) the magnetic gradient force  $\mathbf{f}_{\nabla B}$  and (d) the buoyancy force  $\mathbf{f}_g$  near a conical cathode under the influence of an external vertical magnetic field  $B_0$ . (b) Vectors and color contours of the magnetic flux density  $\mathbf{B}$  near a single Fe cone (diameter 2mm, tip angle  $60^\circ$ ,  $B_0 = 200$  mT; simulation result).

53

54 If the deposition is performed in an inhomogeneous magnetic field, the gradient  
 55 of the magnetic field gives rise to a magnetic gradient force, which may also cause  
 56 electrolyte flow and thus affect the deposition processes. If the length scale over  
 57 which the magnetic field changes is small, e.g. below 1 mm, a strong field gradient  
 58 is created, and the magnetic gradient force may even dominate over the Lorentz  
 59 force [33]. In the case of the ferromagnetic layers studied here, the field gradient is  
 60 caused by the magnetization of the cones distorting the uniform external magnetic  
 61 field. Figure 1(b) shows the magnetic field distribution near a Fe cone in the vertical  
 62 center plane when a uniform external vertical field of 200 mT is applied. Here, the  
 63 magnetization of the Fe cone has not yet completely reached the saturation level  
 64 [36], and large magnitudes of magnetic induction are visible near the tip, creating

65 strong field gradients. The magnetic gradient force is given as [33]:

$$\mathbf{f}_{\nabla\mathbf{B}} = \chi_{\text{sol}}/\mu_0(\mathbf{B} \cdot \nabla)\mathbf{B}, \quad \chi_{\text{sol}} = \sum_i \chi_i^{\text{mol}}c_i + \chi_{\text{H}_2\text{O}} \quad (2)$$

66 Here,  $\mu_0 = 4\pi \cdot 10^{-7} \text{Vs}/(\text{Am})$ ,  $c_i$ ,  $\chi_i^{\text{mol}}$ ,  $\chi_{\text{H}_2\text{O}}$  and  $\chi_{\text{sol}}$  denote the vacuum perme-  
67 ability, the concentration and the molar magnetic susceptibility of species  $i$ , and the  
68 magnetic susceptibilities of water and the solution, respectively.

69 It has been pointed out previously that for electrodeposition performed in a  
70 closed electrochemical cell bounded by walls, the potential parts of forces are bal-  
71 anced by the wall pressure and cannot drive electrolyte flow [30]. Therefore, with  
72 respect to  $\mathbf{f}_{\nabla\mathbf{B}}$  studied here, the rotational part is responsible for the resulting flow  
73 [33]:

$$\nabla \times \mathbf{f}_{\nabla\mathbf{B}} = \frac{1}{2\mu_0} \left( \sum_i \chi_i^{\text{mol}} \nabla c_i \right) \times (\nabla B^2) \quad (3)$$

74 Thus, the flow forced by  $\mathbf{f}_{\nabla\mathbf{B}}$  is determined by the gradients of the species concen-  
75 trations and of the magnetic field. As the concentration gradient near the cathode  
76 develops with ongoing deposition, the magnitude and direction of  $\mathbf{f}_{\nabla\mathbf{B}}$  will vary over  
77 time. Fig. 1 (c) shows a possible flow pattern caused by  $\mathbf{f}_{\nabla\mathbf{B}}$ .

78 Beside the magnetic forces, the buoyancy force which arises from variations in  
79 the density of the electrolyte may also cause electrolyte flow during electrodeposition  
80 [37]:

$$\mathbf{f}_{\mathbf{g}} = (\rho - \rho_0)\mathbf{g} \quad (4)$$

81 Here,  $\rho$ ,  $\rho_0$  and  $\mathbf{g} = -9.81\text{m/s}^2 \mathbf{e}_z$  denote the local and the bulk density of the elec-  
82 trolyte and the vector of the gravitational acceleration which points in a downward  
83 direction  $-\mathbf{e}_z$  (see Fig. 2 for the coordinate system). Density variations originate  
84 from a spatially varying electrolyte composition caused by electrode reactions or  
85 from temperature variations in the electrolyte caused by Ohmic heating. However,  
86 the thermal effect is often much smaller than the solutal one and can be safely  
87 neglected, see Section 2.3.

88 In the following we consider electrochemical cells where the cathode is placed  
89 at the bottom. The metal deposition at the cathode reduces the density of the  
90 electrolyte, and solutal buoyancy tends to bring upward the lighter electrolyte, as  
91 shown in Fig. 1(d). As the cathodes considered are not planar in shape, even in  
92 the case of homogeneous deposition,  $\mathbf{f}_{\mathbf{g}}$  has a non-zero rotational part, which drives  
93 a horizontal flow towards the foot of the cone and an upward flow along the cone  
94 surface:

$$\nabla \times \mathbf{f}_{\mathbf{g}} = g \nabla \rho \times \mathbf{e}_z \quad (5)$$

95 As the deposition starts, this flow sets in unconditionally, which is different from  
96 solutal convection at planar horizontal electrodes; this requires a critical Rayleigh  
97 number to start [38]. The upward flow along the cone can be expected to generate a

98 concentration boundary layer of growing thickness. Thus, near the cone tip, the con-  
99 centration gradient and diffusive mass transfer may be weakened, and cone growth  
100 supported by only the geometrical non-uniformity of the cathode may be impeded.  
101 In this respect, properly adjusted magnetic fields offer the possibility to force an  
102 opposing flow that is strong enough to compensate for the unfavorable buoyancy  
103 flow and thus to enhance the desired structuring effect.

104 Extending the reflections to include planar cathodes with several conical eleva-  
105 tions (see Fig. 2), the flow generated near each single cone may interact with flow  
106 originating from its neighbors. Corresponding damping of the azimuthal flow near  
107 magnetically templated electrodes was already reported in [39]. However, the neigh-  
108 bor influence on the magnetization, the resulting magnetic gradient force and also  
109 the impact of buoyancy has not been studied so far.

110 This work aims at studying the utilization of magnetic fields for the electrode-  
111 position of conically structured ferromagnetic deposits. Although the majority of  
112 today’s practical applications are for micro- and nano-sized conical structures, here  
113 we perform first investigations on a larger scale to gain a basic understanding of  
114 the magnetic field effects. This work extends the earlier study related to Lorentz  
115 force effects with single cones [1] and firstly elaborates on the magnetic gradient  
116 force, which plays an important role at ferromagnetic layers. The study includes  
117 single cones of different shapes and also the influence of neighboring cones at varying  
118 distances from one another. Thus, a detailed understanding is gained of the contri-  
119 butions made by the different forces involved during electrodeposition in a vertical  
120 magnetic field.

## 121 **2. Methods**

### 122 *2.1. Problem description and simulation approach*

123 We perform transient numerical simulations for the galvanostatic electrodeposi-  
124 tion of metal on planar cathodes with periodic arrangements of conical elevations.  
125 The electrodes are oriented horizontally, and the electrochemical cell is exposed to  
126 a uniform magnetic field which is oriented vertically. We consider cathodes made of  
127 iron and additionally also of copper, to compare with earlier investigations at dia-  
128 magnetic electrodes [1]. In order to study the basic effects of both magnetic forces,  
129 as well as the influence of neighbor effects, we start with cones of mm size, which  
130 will also facilitate the later experimental validation of our simulation results. The  
131 deposition times considered are in the range of minutes. We can therefore neglect  
132 changes of the electrode shape during deposition and treat the electrode geometry  
133 as fixed. Hence, the magnetic field near the electrodes also does not change during  
134 deposition. In order to further exclude any possible influence from the different re-  
135 action kinetics of the metals deposited, we deposit copper at both the ferromagnetic

136 and the diamagnetic cathodes. We also neglect any possible side reactions such as  
137 the hydrogen evolution reaction.

138 Our simulation approach consists of three steps which are outlined in Fig. 2. In  
139 the first step, we study the generic behavior at single cones and neglect any influence  
140 from neighboring cones, which are assumed to be far away. Thus, in a cylindrical  
141 region with the cone placed in the center of the cathode, the problem can be assumed  
142 to be axisymmetrical. The computational domain is thus the vertical plane bounded  
143 by the symmetry axis and the outer mantle boundary, and by the electrodes (see  
144 Fig. 2(a-b)). The simulations allow for an azimuthal flow caused by the Lorentz  
145 force, but neglect any dependencies on the azimuthal ( $\theta$ ) position.

146 In the second step, we take neighbor effects into account. We consider an in-  
147 finitely extended planar cathode with a regular checkerboard arrangement of conical  
148 deformations (see Fig. 2(c-d)). In the following we assume that the electrodeposition  
149 proceeds identically at all cones. Global effects originating from e.g. recirculating  
150 flows around electrodes of finite size [28] are beyond the scope of this study. We  
151 therefore pick a cuboid computational domain between the electrodes where the  
152 cone is located in the center of the cathode square. The side length of the square  
153 corresponds to the cone distance, which will be varied later to study different cone  
154 densities. At the opposite vertical faces of the cuboid domain, periodic boundary  
155 conditions will be applied in the simulations.

156 As these simulations have to be performed in 3D and are expensive in terms  
157 of computing resources, in the third step, we introduce an approximate scheme  
158 for considering the neighbor influence. In order to facilitate simpler axisymmetric  
159 simulations, we assume that there are neighboring cones at the same distance for all  
160 azimuthal directions. Thus, the cylindrical domain shown in Fig. 2(a-b) can be used  
161 again. Here, in contrast to Step 1, the radial extension is defined as half the distance  
162 between the cones. At this outer domain boundary, for reasons of symmetry, the flow  
163 has no radial component, and the azimuthal component originating from the Lorentz  
164 force can be expected to be canceled out, as the azimuthal flow direction is opposite  
165 between neighbors. This approximation allows 2D simulations to be performed  
166 instead of 3D simulations as a means of considering the influence of neighboring  
167 cones, and will be validated below by presenting a comparison of the two simulation  
168 approaches for the case of the copper cones. The boundary conditions applied in  
169 the three steps will be explained in full detail in Section 2.2.

## 170 *2.2. Model equations and boundary conditions*

171 The numerical model consists of a coupled system of equations for the magnetic  
172 field, the electrolyte velocity, the concentration of the ionic species and the electric  
173 field. The computational domains for the three steps of the simulations are outlined  
174 in Fig. 2(b)(d), and the boundary conditions applied are summarized in Table 1.

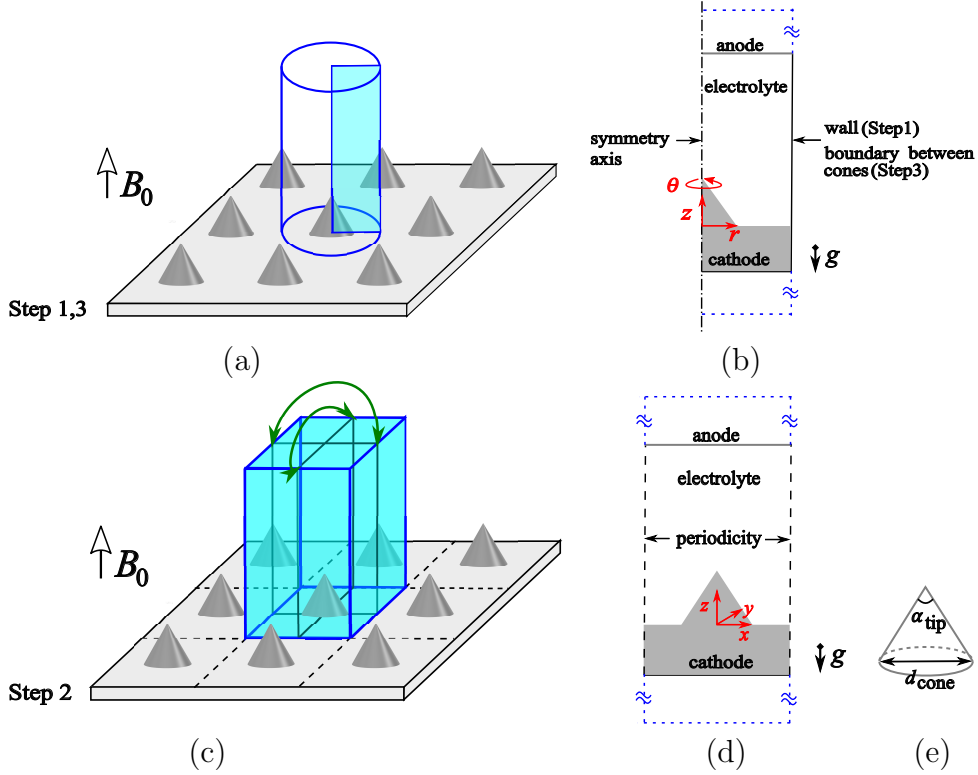


Figure 2: Sketch of the computational domains (marked in light blue), the related coordinate systems (cylindrical in (b) and Cartesian in (d)) and the specific boundary conditions applied to illustrate the three steps of the computational approach. (a-b) Step 1 and Step 3. (c-d) Step 2. At the opposite vertical faces of the cuboid, green arrows indicate the periodic boundary conditions which are applied. The dashed blue lines indicate the vertically extended domains for calculating the magnetic field. (e) Sketch of the cone geometry with  $\alpha_{\text{tip}}$  and  $d_{\text{cone}}$  denoting the cone tip angle and the cone diameter. For more details see Sections 2.1 and 2.2.

175 The magnetic field is obtained by solving the Maxwell equations [40]:

$$\nabla \cdot \mathbf{B} = 0, \quad \nabla \times \mathbf{H} = 0 \quad (6)$$

176 The magnetic field strength  $\mathbf{H}$  is linearly related to the magnetic flux density  $\mathbf{B}$  by  
 177 the vacuum permeability  $\mu_0$  for the paramagnetic and diamagnetic materials in our  
 178 calculations, i.e.  $\mathbf{B} = \mu_0 \mathbf{H}$ . Inside the ferromagnetic cathodes, there is

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \quad (7)$$

179 Here, the magnetization  $\mathbf{M}$  is given by a corresponding magnetization curve  
 180 [41].  $\mathbf{H}$  is the sum of the external field strength ( $\mathbf{B}_0/\mu_0$ ) and the demagnetizing  
 181 field, the latter being directed antiparallel to  $\mathbf{M}$  in ferromagnetic materials [42].  
 182 We apply  $\mathbf{B} = \mathbf{B}_0$  on the outer horizontal boundaries of the magnetic field domain  
 183 for all three steps and at the vertical side wall of Step 1, because a homogeneous  
 184 external magnetic field is imposed on the cell. For Steps 2 and 3, the neighboring  
 185 effects imply symmetry conditions at the vertical boundaries between the cones. We  
 186 therefore apply periodic conditions at the oppositely located vertical boundaries of  
 187 the cuboid domain in Step 2, and  $\mathbf{B} \cdot \mathbf{n} = 0$  at the outer radius in Step 3. Here  $\mathbf{n}$



188 denotes the unit vector normal to the boundary. It should be mentioned that the  
 189 magnetic boundary conditions applied here exclude specific deposition effects at the  
 190 outer edges of the planar part of the ferromagnetic electrode found elsewhere [16].

191 The electrolyte velocity  $\mathbf{U}$  is obtained by solving the Navier-Stokes equations  
 192 including the volume forces mentioned above and complemented by the incompress-  
 193 ibility constraint,

$$\rho_0 \left( \frac{\partial \mathbf{U}}{\partial t} + (\mathbf{U} \cdot \nabla) \mathbf{U} \right) = -\nabla P + \mu \nabla^2 \mathbf{U} + \mathbf{f}_L + \mathbf{f}_{\nabla B} + \mathbf{f}_g, \quad \nabla \cdot \mathbf{U} = 0 \quad (8)$$

194 Here,  $P$  and  $\mu$  denote the dynamic pressure and the dynamic viscosity of the elec-  
 195 trolyte. A no-slip boundary condition is applied at the electrodes for all steps and  
 196 at the vertical side wall for Step 1. For Step 2, periodic boundary conditions are  
 197 enforced at the vertical boundaries. For Step 3, symmetry with respect to the neigh-  
 198 bor influence allows a free-slip boundary condition to be applied ( $\mathbf{U} \cdot \mathbf{n} = 0$ ) at the  
 199 outer radius, supplemented by the constraint that the azimuthal velocity ( $U_\theta$ ) has  
 200 to vanish.

201 The distribution of species in the electrolyte is obtained by solving the Nernst-  
 202 Planck equations of dilute solutions:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i \quad (9)$$

203 Here,  $\mathbf{N}_i$  denotes the flux density of species  $i$

$$\mathbf{N}_i = -z_i F \frac{D_i}{RT} c_i \nabla \phi - D_i \nabla c_i + c_i \mathbf{U} \quad (10)$$

204 which, beside transport by migration and diffusion, also includes convective trans-  
 205 port by the electrolyte velocity from Eq. (8) [37]. Here,  $z_i$ ,  $D_i$ ,  $F$ ,  $R$ ,  $T$  and  $\phi$  are the  
 206 charge number and the diffusion coefficient of species  $i$ , the Faraday constant, the  
 207 universal gas constant, the temperature and the electric potential, respectively. The  
 208 electric current density in the solution is the net flux density of all charged species:

$$\mathbf{j} = F \sum_i z_i \mathbf{N}_i \quad (11)$$

209 We further assume electroneutrality in the electrolyte, i.e.  $\sum z_i c_i = 0$ . Combining  
 210 Eqs. 10, 11 and the conservation of charge ( $\nabla \cdot \mathbf{j} = 0$ ), the electric potential can be  
 211 obtained as the solution of a Poisson equation:

$$\nabla \cdot \left( -F^2 \nabla \phi \sum_i z_i^2 \frac{D_i c_i}{RT} \right) - \nabla \cdot \left( F \sum_i z_i D_i \nabla c_i \right) = 0 \quad (12)$$

212 Regarding the boundary conditions applied, on electrically passive walls, due to  
 213 electric insulation, the normal components of the electric current and the flux of all

214 ionic species have to vanish for Step 1. The same boundary conditions are applied  
 215 for Step 3, but for reasons of symmetry. For Step 2, periodic boundary conditions  
 216 are again implemented. On the electrodes, a Butler-Volmer relation is applied to  
 217 describe the kinetics of the copper reaction for all three steps [37]:

$$j_n = j_0 \left( \exp \left( \frac{\alpha_a F \eta_s}{RT} \right) - \exp \left( \frac{-\alpha_c F \eta_s}{RT} \right) \right) \quad (13)$$

218 Here  $j_0$ ,  $\alpha_a$  and  $\alpha_c$  denote the exchange current density and the apparent transfer  
 219 coefficients. The surface overpotential  $\eta_s$  is defined as the potential of the electrode  
 220  $\phi_e$  relative to the solution potential  $\phi$  minus the equilibrium electrode potential  
 221  $\phi_{eq}$  given by the Nernst equation, i.e.  $\eta_s = \phi_e - \phi - \phi_{eq}$  [37]. In the simulations,  
 222 the electrode potential is adjusted at each time step to satisfy the galvanostatic  
 condition  $I = I(\phi_e) = const.$

Table 1: Boundary conditions applied in the different steps of the simulations. The subscripts  
 "src" and "dst" denote the source and the destination boundaries in the case of periodic boundary  
 conditions (see Fig. 2 (c-d)).

	Boundary	Step 1	Step 2	Step 3
Magnetic field	Axis	$\partial \mathbf{B} / \partial r = 0$	-	$\partial \mathbf{B} / \partial r = 0$
	Vertical	$\mathbf{B} = \mathbf{B}_0$	$\mathbf{B}_{src} = \mathbf{B}_{dst}$	$\mathbf{B} \cdot \mathbf{n} = 0$
	Horizontal	$\mathbf{B} = \mathbf{B}_0$		
Electrolyte velocity	Axis	$\partial \mathbf{U} / \partial r = 0$	-	$\partial \mathbf{U} / \partial r = 0$
	Vertical	$\mathbf{U} = \mathbf{0}$	$\mathbf{U}_{src} = \mathbf{U}_{dst}$	$\mathbf{U} \cdot \mathbf{n} = 0, U_\theta = 0$
	Electrodes	$\mathbf{U} = \mathbf{0}$		
Electric field	Axis	$\partial \mathbf{j} / \partial r = 0$	-	$\partial \mathbf{j} / \partial r = 0$
	Vertical	$\mathbf{j} \cdot \mathbf{n} = 0$	$\mathbf{j}_{src} = \mathbf{j}_{dst}$	$\mathbf{j} \cdot \mathbf{n} = 0$
	Electrodes	$\mathbf{j} \cdot \mathbf{n}$ from Eq. 13		
Species	Axis	$\partial \mathbf{N}_i / \partial r = 0$	-	$\partial \mathbf{N}_i / \partial r = 0$
	Vertical	$\mathbf{N}_i \cdot \mathbf{n} = 0$	$\mathbf{N}_{i,src} = \mathbf{N}_{i,dst}$	$\mathbf{N}_i \cdot \mathbf{n} = 0$
	Electrodes	Passive ions: $\mathbf{N}_i = 0$ Active ions: $\mathbf{N}_i \cdot \mathbf{n}$ from Eq. 11, Eq. 13		

223

### 224 2.3. Material and simulation parameters

225 The material parameters for solving Eqs. 8-13 are listed in Table 2. The elec-  
 226 trolyte is an aqueous 0.1 M  $\text{CuSO}_4$  solution at room temperature. Because of elec-  
 227 trical neutrality, it holds that  $c_{\text{Cu}^{2+}} = c_{\text{SO}_4^{2-}}$ , and the species index  $i$  can be omitted  
 228 in the following. With respect to the reaction kinetics of copper, the exchange cur-  
 229 rent density  $j_0$  is given as  $j_0 = j_{00} (c_s/c_0)^\gamma$ , with  $c_s$  and  $c_0$  denoting the surface and  
 230 the bulk concentration of the electroactive  $\text{Cu}^{2+}$  species. The reference exchange  
 231 current density  $j_{00}$  and the kinetic parameter  $\gamma$  are taken from [43]. In the simu-  
 232 lations performed, we found that the influence of the concentration-related term of  
 233 the Nernst equation on the surface overpotential is negligibly small. We therefore  
 234 take  $\phi_{eq}$  to be equal to the standard equilibrium potential,  $\phi_{eq,0}$ , which reduces the  
 235 non-linearity of the boundary condition.

236 The simulation parameters are summarized in Table 3. For the single cone  
 237 studies of Step 1, a cone is considered with a base diameter of  $d_{\text{cone}} = 2$  mm and a  
 238 tip angle of  $\alpha_{\text{tip}} = 60^\circ$ . These dimensions are varied only in the cone shape studies,  
 239 see Section 3.2. The chosen cell height of 30 mm is large enough to avoid any  
 240 influence from the anodic mass transfer at the cathode. The radial extension of the  
 241 electrochemical cell is chosen to be  $5 d_{\text{cone}}$ , which is large enough to ensure that the  
 242 flow forced near the cone is not affected by the side wall. The current density used  
 243 for the simulations in the three steps varies between 8 and 16 mA/cm<sup>2</sup>. In order to  
 244 obtain comparable amplitudes of the Lorentz force, the magnetic field amplitude is  
 245 accordingly adjusted between 200 and 400 mT.

246 We now come back to estimating the relative significance of thermal and solutal  
 247 buoyancy. For the maximum current density considered, of 16 mA/cm<sup>2</sup>, when the  
 248 Joule heat is assumed to be completely transferred to the electrolyte, the local tem-  
 249 perature rises by about 0.2 K within one minute. The corresponding thermal density  
 250 variation is less than 0.01% [44, 45]. However, assuming there is a concentration  
 251 variation of 0.1 M, the solutal density variation is more than 100 times larger and  
 252 reaches about 1.6% [45, 46]. Thermal buoyancy can therefore safely be neglected  
 253 in the following. As the solutal density variation is still small, we may apply the  
 254 Boussinesq approximation [38], and the buoyancy force expressed by Eq. 4 can be  
 255 simplified to:

$$\mathbf{f}_g = \rho_0 \mathbf{g} \beta_{\text{CuSO}_4} (c - c_0) \quad (14)$$

with  $\beta_{\text{CuSO}_4}$  denoting the volume expansion coefficient of the electrolyte (Table 2).

Table 2: Material parameters for 0.1 M CuSO<sub>4</sub> at room temperature.

$\chi_{\text{Cu}^{2+}}^{\text{mol}}$ (m <sup>3</sup> /mol)	$1.57 \cdot 10^{-8}$	[32]
$\chi_{\text{H}_2\text{O}}$	$-9.0 \cdot 10^{-6}$	
$\rho_0$ (kg/m <sup>3</sup> )	1014	
$\beta_{\text{CuSO}_4}$ (m <sup>3</sup> /mol)	$1.6 \cdot 10^{-4}$	[46]
$\mu$ (Pa · s)	$1.04 \cdot 10^{-3}$	
$D_{\text{Cu}^{2+}}$ (m <sup>2</sup> /s)	$5.6 \cdot 10^{-10}$	[43]
$D_{\text{SO}_4^{2-}}$ (m <sup>2</sup> /s)	$10.04 \cdot 10^{-10}$	
$z_{\text{Cu}^{2+}}$	2	
$z_{\text{SO}_4^{2-}}$	-2	
$j_{00}$ (mA/cm <sup>2</sup> )	10	
$\phi_{\text{eq},0}$ (V)	0.337	
$\gamma$	0.42	[37, 43]
$\alpha_a$	1.5	
$\alpha_c$	0.5	

256

#### 257 2.4. Numerical details and validations

258 The simulations were performed using the Finite Element software package Com-  
 259 sol V.5.5 [41]. Second-order shape functions are used for the magnetic field  $\mathbf{B}$ , the

Table 3: Simulation parameters.

	Step 1			Step 2	Step 3
	30°	60°	90°	60°	60°
$\alpha_{\text{tip}}$	30°	60°	90°	60°	60°
$d_{\text{cone}}$ (mm)	1.4	2	2.4	2	2
Cone surface area (mm <sup>2</sup> )	6.28			6.28	6.28
Cell height (mm)	30			30	30
Height of magnetic field domain (mm)	100			100	100
Cell width (mm)	10			-	-
Cone distance ( $d_{\text{cone}}$ )	-			1.5, 2, 3, 5	1.5, 2, 3, 5
$j_{\text{cathode,avg}}$ (mA/cm <sup>2</sup> )	16			8	8
$B_0$ (mT)	200			400	400
$c_0$ (M)	0.1			0.1	0.1

260 velocity  $\mathbf{U}$ , the concentration  $c$  and the electric potential  $\phi$ , and first-order shape  
261 functions are used for the pressure  $P$ . The initial conditions for the transient sim-  
262 ulations are an electrolyte with a homogeneous bulk concentration  $c_0$  at rest, i.e.  
263  $\mathbf{U} = 0$ . Time integration was carried out using an implicit backward differentiation  
264 formula method of up to the second order. The time step is adjusted by the solver  
265 based on error estimation during the calculations, with an upper limit of 0.1 s which,  
266 according to a time-step study, ensures the accuracy of the results.

267 Unstructured triangular (2D) or prismatic (3D) meshes were generated and re-  
268 fined near the boundaries so as to sufficiently resolve the spatial gradients of the  
269 concentration, the velocity and the magnetic field. A mesh study has shown that  
270 the steep magnetic field gradients near the Fe cones are most demanding. Thus,  
271 the mesh size near the cone surface was chosen to be  $0.0005 d_{\text{cone}}$  for the Fe cones  
272 and  $0.001 d_{\text{cone}}$  for the Cu cones, respectively. This choice also ensures the sufficient  
273 resolution of the concentration and velocity boundary layers.

274 For the magnetic field, a domain size study was performed to ensure that the  
275 proximity of the top and bottom boundary does not affect the field distribution inside  
276 the electrochemical cell. The magnetic field distributions obtained numerically have  
277 further been validated with experimental data for different magnet geometries [1].  
278 As a result, a domain height of 100 mm was chosen.

279 The full numerical model described above was validated by experimental data  
280 from a similar deposition process on a single Cu cone [1] and also by deposition  
281 problems at magnetically templated electrodes, where the magnetic gradient force  
282 is of importance [33, 34]. As a result, the numerical model is able to deliver accu-  
283 rate, reliable information on the magnetic field distribution, the electrolyte flow, the  
284 species distribution and the current density distribution in the cell.

### 285 3. Results and Discussion

#### 286 3.1. Single cones

287 In the following, the generic case of single cones (Step 1) is considered in order to  
 288 obtain a basic understanding of the influence of the different volume forces involved  
 289 in the deposition process. An intermediate tip angle of  $60^\circ$  is chosen for the copper  
 290 and iron cones investigated. Fig. 3 shows the azimuthal flow driven by the Lorentz  
 291 force  $\mathbf{f}_L$  after a deposition time of 10 s. Surprisingly, an opposite direction of rotation  
 292 is observed for the iron cone compared to the copper cone. Moreover, the azimuthal  
 293 flow for the iron cone extends over a smaller area than for the copper cone. This  
 294 can be understood by considering the Lorentz force of the axisymmetric problem,  
 295 which consists of an azimuthal component only:

$$\mathbf{f}_L = (j_z B_r - j_r B_z) \mathbf{e}_\theta \quad (15)$$

296 Here,  $\mathbf{e}_\theta$  denotes the unity vector in the azimuthal direction (Fig. 2(b)). In general,  
 297 when approaching the cone, the vertical current density vectors bend towards the  
 298 surface-normal direction of the cone. Thus,  $j_r < 0$ ,  $j_z < 0$ . For the Cu case, the  
 299 magnetic field is not modified by the diamagnetic cathode, and the magnetic field  
 300 equals the external vertical field applied, i.e.  $B_r = 0$ ,  $B_z = B_0$ . Therefore, as shown  
 301 on the right-hand side of Fig. 3,  $j_r B_0 < 0$  is responsible for the anticlockwise  
 rotation seen from the top of the cell.

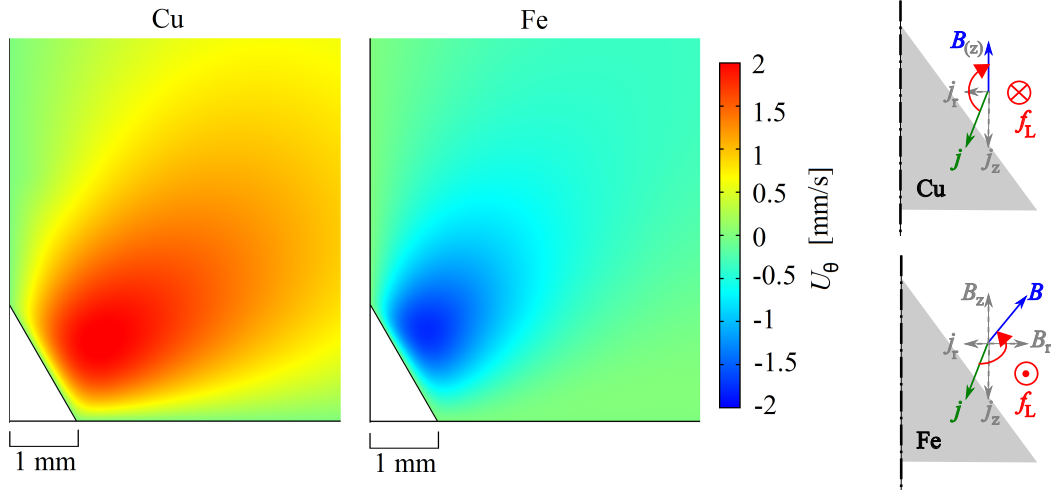


Figure 3: Color surface of the azimuthal velocity after 10 s deposition time near the Cu and the Fe cones ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 16 \text{ mA/cm}^2$ ,  $B_0 = 200 \text{ mT}$ ). The direction of azimuthal forcing by the Lorentz force is outlined on the far right.

302

303 For the Fe case, the magnetic field is modified in the vicinity of the cone due to its  
 304 magnetization, as shown in Fig. 1. Unlike the Cu case, radial components of  $\mathbf{B}$  give  
 305 rise to negative force amplitudes  $j_z B_r$  which may exceed the positive part ( $-j_r B_z$ ).  
 306 The resulting clockwise forcing is shown on the right-hand side of Fig. 3. As large  
 307 radial components of the magnetic field are only found close to the surface of the

308 magnetized cone, the region of rotation is smaller compared to the Cu case. Similar  
 309 clockwise rotation was also found for the steeper and flatter iron cones investigated  
 310 in Section 3.2. However, it should be noted that, irrespective of the direction of the  
 311 azimuthal flow, the secondary flow created by the centrifugal force is always directed  
 312 downwards towards the cone tip [33, 39].

313 Fig. 4 compares the meridional velocity near the Cu and Fe cones with and  
 314 without a magnetic field after 5 s and 10 s of deposition time. In the absence of the  
 315 magnetic field, the behavior is identical for Cu and Fe cones. An upward-directed  
 316 buoyant flow develops with ongoing deposition, reaching a velocity of about 1 mm/s  
 317 above the cone after 10 s of deposition. Similar flow pattern were found in an earlier  
 318 study of copper deposition at a copper cone in a weak vertical magnetic field of  
 319 60 mT. There, the downward acceleration generated by the Lorentz force was not  
 320 strong enough to reverse the direction of flow, and the concentration boundary layer  
 was advected upwards and detached at the cone tip [1]. In the following, a stronger

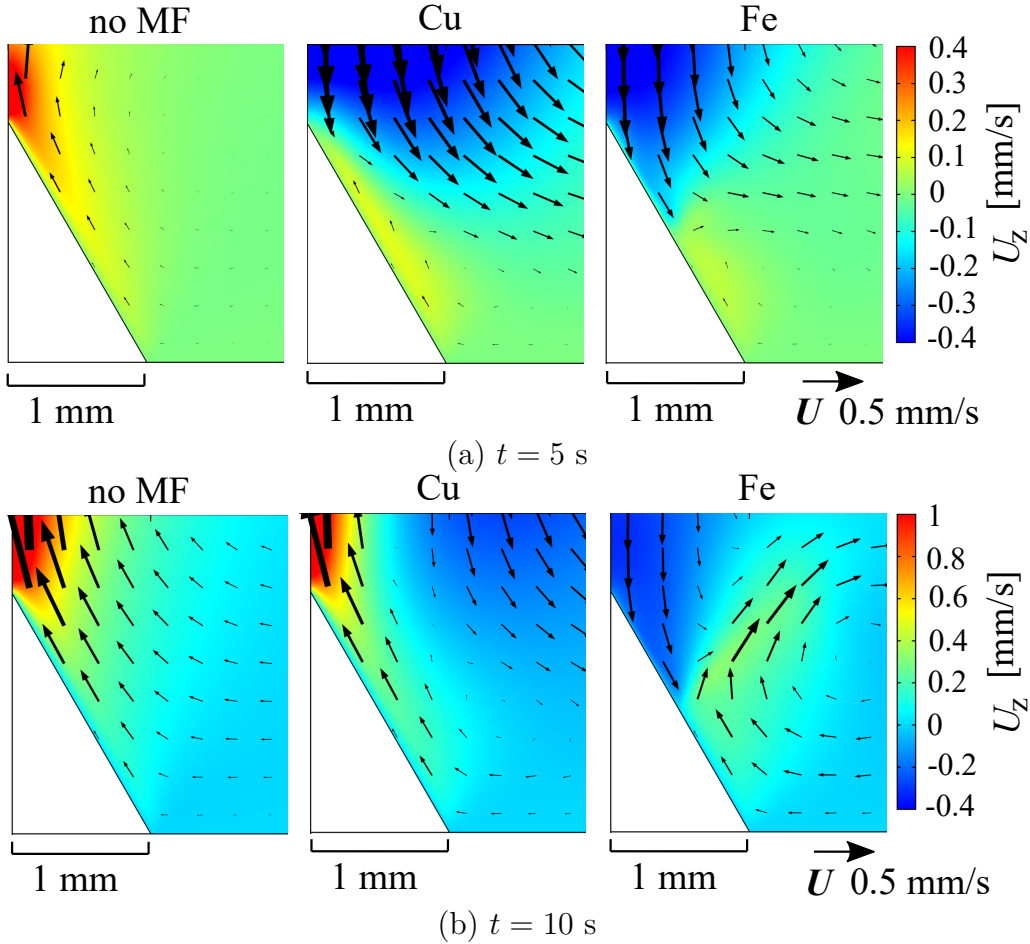


Figure 4: Color surface of the vertical velocity after 5 s and 10 s deposition time near a cone without a magnetic field (left: no MF), near the Cu cone with a magnetic field (middle) and the Fe cone with a magnetic field (right).  $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 16$  mA/cm<sup>2</sup>,  $B_0 = 200$  mT. Black arrows represent the meridional velocity vectors.

321

322 magnetic field of 200 mT is considered. As shown in Fig. 4, near the copper cone  
 323 after a deposition time of 5 s a strong downward-directed flow is clearly visible,  
 324 which can be attributed to the dominant secondary flow caused by the Lorentz

325 force. However, the flow direction very close to the cone surface has already turned  
 326 upwards due to the buoyancy of the concentration boundary layer, indicated by the  
 327 yellow region. As the deposition continues, the buoyant flow accelerates with time.  
 328 As shown after 10 s, the direction of flow near the surface of the cone is dominated  
 329 by buoyancy, which causes the concentration boundary layer to detach from the tip  
 330 of the cone. A weak downward flow remains at a larger distance from the cone.

331 For the Fe cone in the magnetic field, the magnetic gradient force  $\mathbf{f}_{\nabla\mathbf{B}}$  also comes  
 332 into play. In comparison to the copper case, the downward flow close to the cone  
 333 surface seems to be stronger. After 5 s, the downward flow along the upper cone  
 334 region is clearly visible, whereas the flow velocity near the lower part of the cone is  
 335 low. After 10 s of deposition, the downward flow along the upper cone region is still  
 336 maintained, but an upward flow caused by buoyancy is clearly visible in the lower  
 337 part. This results in a jet-like flow leaving the cone surface in an approximately  
 338 normal direction at about half the height of the cone. Although the influence of  $\mathbf{f}_{\mathbf{L}}$   
 339 in the case of the iron cone is slightly weaker than in the case of the copper cone,  
 340  $\mathbf{f}_{\nabla\mathbf{B}}$  is effectively counteracting  $\mathbf{f}_{\mathbf{g}}$  in the vicinity of the cone surface.

341 In order to further analyze the influence of  $\mathbf{f}_{\nabla\mathbf{B}}$  on the deposition process,  
 342 Figs. 5(a-b) show the concentration of the copper ions close to the iron cone after a  
 343 deposition time of 5 s and 10 s. The images are superimposed with the meridional  
 344 velocity vectors. The downward flow along the surface of the upper part of the cone  
 345 continuously brings fresh bulk electrolyte to the tip, keeping the local concentration  
 346 boundary layer thin. By contrast, the upward buoyant flow already originates at  
 347 the horizontal part of the cathode, with a horizontal flow towards the cone, and the  
 348 thickness of the concentration boundary layer there grows with time. The aforemen-  
 349 tioned jet-like flow about halfway up the cone is accompanied by the corresponding  
 350 detachment and advection of the concentration boundary layer in an approximately  
 351 electrode-normal direction. A similar effect of boundary layer separation caused  
 352 by the opposing action of  $\mathbf{f}_{\mathbf{L}}$  and  $\mathbf{f}_{\mathbf{g}}$  during electrodeposition was already reported  
 353 elsewhere [47].

354 The concentration boundary layer near the cone, in turn, affects  $\mathbf{f}_{\nabla\mathbf{B}}$  and thus  
 355 the flow field. Applying Eq. 2, based on the material parameters given in Table  
 356 2, the magnetic susceptibility of the bulk solution is negative, as the diamagnetic  
 357 contribution of the water molecules dominates [32]:

$$\chi_{\text{sol}} = \chi_{\text{Cu}^{2+}}^{\text{mol}} c_0 + \chi_{\text{H}_2\text{O}} = -7.43 \cdot 10^{-6} \quad (16)$$

358 This also holds inside the concentration boundary layer, where  $c_{\text{Cu}^{2+}} \leq c_0$  can be  
 359 assumed. Therefore,  $\mathbf{f}_{\nabla\mathbf{B}}$  is acting in the opposite direction to that of the magnetic  
 360 gradient. As the strongest magnetic field is found near the tip of the cone,  $\mathbf{f}_{\nabla\mathbf{B}}$   
 361 points away from the tip. However, this contradicts the simulation result, which  
 362 indicates that the electrolyte flow is directed towards the tip. This issue can easily

363 be resolved by only considering the rotational parts of the magnetic gradient force  
 364 and the buoyancy force, as discussed in the introduction. As axisymmetry applies,  
 365 the curl of both forces defined in Eqs. 3 and 5 in cylindrical coordinates reads:

$$\nabla \times \mathbf{f}_{\nabla B} = \frac{\chi^{\text{mol}}}{\mu_0} \left( \frac{\partial c}{\partial z} B \frac{\partial B}{\partial r} - \frac{\partial c}{\partial r} B \frac{\partial B}{\partial z} \right) \mathbf{e}_\theta \quad (17)$$

366

$$\nabla \times \mathbf{f}_g = \beta_c g \rho_0 \left( \frac{\partial c}{\partial r} \right) \mathbf{e}_\theta \quad (18)$$

367 Near the cone surface, the concentration gradient vector essentially points away  
 368 from the surface into the electrolyte volume, i.e.  $\frac{\partial c}{\partial r} > 0$ ,  $\frac{\partial c}{\partial z} > 0$  (see Fig. 5(b)).  
 369 As the maximal magnetic field exists near the cone tip, along the cone surface  
 370  $\frac{\partial B}{\partial r} < 0$ ,  $\frac{\partial B}{\partial z} > 0$ . According to Eq. 17, the resulting  $\nabla \times \mathbf{f}_{\nabla B}$  has a negative  
 371 azimuthal amplitude and forces the flow to rotate in an anticlockwise direction in  
 372 the meridional plane, i.e. downwards along the cone surface. In contrast,  $\nabla \times \mathbf{f}_g$  has  
 373 a positive azimuthal amplitude along the cone surface because  $\frac{\partial c}{\partial r} > 0$ . As the final  
 374 flow is determined by the curl of both forces, in Fig. 5(c) the sum of  $\nabla \times \mathbf{f}_{\nabla B}$  and  
 375  $\nabla \times \mathbf{f}_g$  is shown after 10 s of deposition time. It can be clearly seen that the upper  
 376 part of the cone boundary layer is dominated by the negative curl of  $\mathbf{f}_{\nabla B}$ , whereas  
 377 the lower part is dominated by the positive curl of  $\mathbf{f}_g$ . This means that a downward  
 378 flow is forced along the surface of the upper cone part, counteracting the upward  
 379 buoyant flow. These flows force the jet-like departure of the concentration boundary  
 380 layer from the cone surface at about mid-height. Thus, the azimuthal components  
 of  $\nabla \times \mathbf{f}_{\nabla B}$  and  $\nabla \times \mathbf{f}_g$  deliver a vivid interpretation of the flow pattern observed.

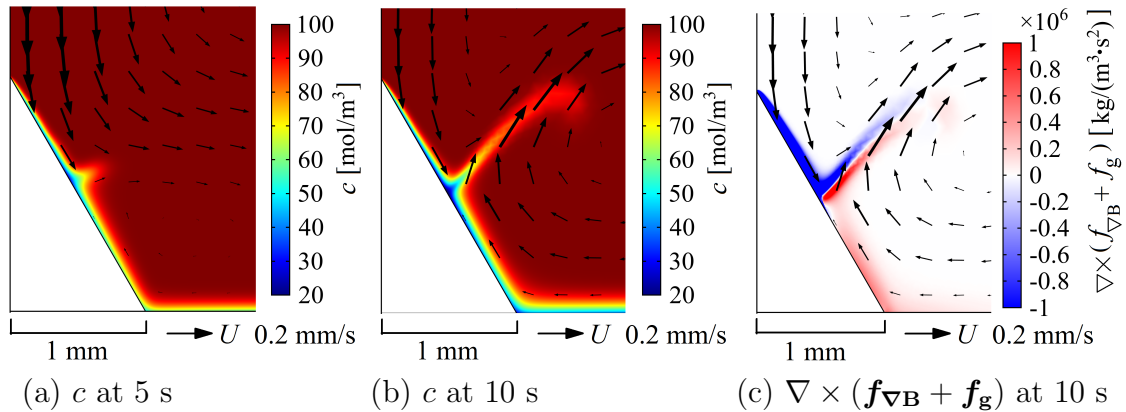


Figure 5: Color surface of the concentration after (a) 5 s and (b) 10 s deposition time and (c) the sum of the curl of the magnetic gradient force and the buoyancy force after 10 s deposition near the Fe cone ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 16 \text{ mA/cm}^2$ ,  $B_0 = 200 \text{ mT}$ ). Black arrows represent meridional velocity vectors.

381

382 The influence of the magnetic forces on the growth dynamics of conical elevations  
 383 on the cathode can be evaluated by considering the deposit thickness along the cone  
 384 surface [37]:

$$d(r, T) = \frac{V_m}{zF} \int_0^T j_n(r, t) dt \quad (19)$$



385 Here,  $V_m = 7.11 \times 10^{-6} \text{ m}^3/\text{mol}$  denotes the molar volume of copper [48], and  $T$   
 386 denotes the deposition time. Fig. 6 shows the initial height contour of the cone  
 387 (left) and the deposit thickness along the surface of the Cu and Fe cones after  
 388 10 s of deposition time (right). In the case without a magnetic field, the deposit  
 389 thickness increases monotonically from the foot to the tip of the cone, as a result of  
 390 the previously mentioned support for cone growth for geometrical reasons. Despite  
 391 the counteraction of the upward buoyant flow discussed above, in total, cone growth  
 would be supported.

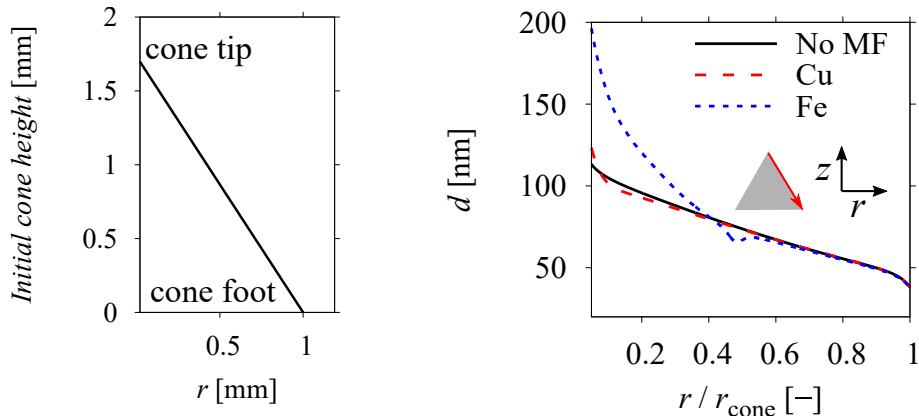


Figure 6: Left: Initial height contour of the cone. Right: Deposit thickness along the cone surface for the cases without magnetic field (No MF) and for Cu and Fe cones in a vertical magnetic field after 10 s deposition time ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 16 \text{ mA/cm}^2$ ,  $B_0 = 200 \text{ mT}$ ). The horizontal axis is the radial surface coordinate normalized by the cone radius  $r_{\text{cone}}$ .

392

393 In the case of the copper cone in the vertical magnetic field, small differences  
 394 are found with respect to the case without a magnetic field. Close to the tip of the  
 395 cone, the thickness of the deposit is increased. This is a result of the downward  
 396 secondary flow caused by  $\mathbf{f}_L$ , which initially supersedes the upward buoyant flow.  
 397 This reversal of the flow direction in the tip region in the first few seconds of the  
 398 deposition enriches the boundary layer and thus enhances mass transfer, see Fig. S1  
 399 in the Supplementary Information (SI). In the region below, down to about half  
 400 the height of the cone, the deposit is slightly thinner in comparison to the case  
 401 without a magnetic field. This suggests that during the deposition period of 10 s,  
 402 the counteraction between the opposing secondary flow and the buoyant flow may  
 403 have briefly led to a thicker boundary layer in the region slightly below the cone tip.  
 404 For a more detailed discussion we refer to section 3.2 and also to Fig. S1 in SI.

405 For the case of the iron cone in the magnetic field, stronger support for cone  
 406 growth is found compared to the case of copper. As can be seen in Fig. 6, the  
 407 deposit thickness in the upper half of the cone is considerably increased and almost  
 408 doubled at the tip compared to the case without a magnetic field. This results  
 409 from a stronger downward flow caused by the additional action of the magnetic  
 410 gradient force  $\mathbf{f}_{\nabla B}$  compared to the case of copper. The local minimum of the  
 411 deposit thickness found at about  $r/r_{\text{cone}} = 0.5$  is related to the detachment of the

412 concentration boundary layer in a jet-like flow, as shown in Fig. 5(b).

413 As a means of further assessing the impact of the different volume forces on  
 414 the deposition process, the ratios of the magnetic forces to the buoyancy force are  
 415 introduced as follows [33]:

$$R_{\text{MHD}} = \frac{\int_V |\mathbf{f}_L| dV}{\int_V |\mathbf{f}_g| dV}, \quad R_{\nabla B} = \frac{\int_V |\mathbf{f}_{\nabla B}| dV}{\int_V |\mathbf{f}_g| dV} \quad (20)$$

416 Here, the integration over volume  $V$  is restricted to the main flow region ( $0 < r <$   
 417  $2.5 d_{\text{cone}}, 0 < z < 2.5 d_{\text{cone}}, 0 < \theta < 2\pi$ ). The temporal behavior of both quantities  
 during the deposition process in the magnetic field is presented in Fig. 7.

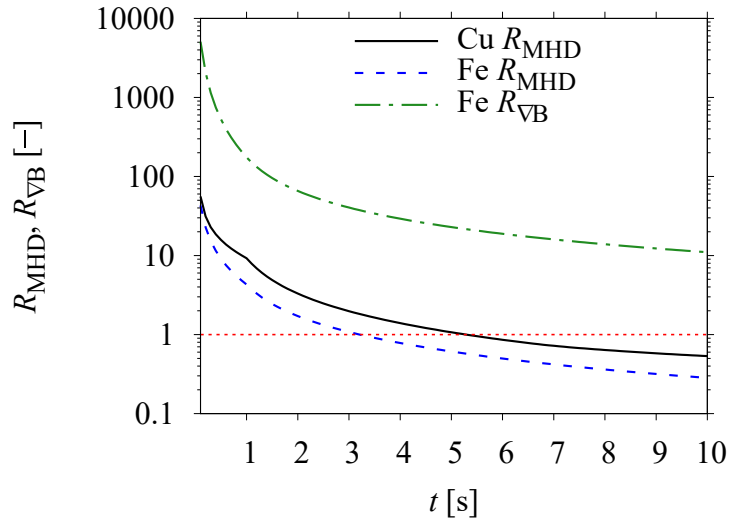


Figure 7: Temporal evolution of the force ratios  $R_{\text{MHD}}$  and  $R_{\nabla B}$  defined in Eq. (20) for deposition on single copper and iron cones ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 16 \text{ mA/cm}^2$ ,  $B_0 = 200 \text{ mT}$ ). The vertical axis is shown on a logarithmic scale for better visibility, the red dashed line indicates the critical value of the force ratio of 1.

418

419 For both copper and iron cones,  $R_{\text{MHD}}$  shows a strong decrease with time. This is  
 420 caused by the different temporal behavior of  $\mathbf{f}_L$  and  $\mathbf{f}_g$ . As a galvanostatic process is  
 421 considered, the current density distribution can be expected to change only slowly  
 422 with ongoing deposition [1]. Therefore,  $\mathbf{f}_L$  is nearly constant, whereas  $\mathbf{f}_g$  grows  
 423 considerably with time due to the development of the concentration boundary layer.  
 424 In the case of copper,  $R_{\text{MHD}}$  sinks below the critical value of unity at  $t \approx 5 \text{ s}$ . This  
 425 is in line with the above discussion of the corresponding electrolyte flow pattern in  
 426 Fig. 4. In comparison, in the case of iron  $R_{\text{MHD}}$  is slightly lower and already drops  
 427 below unity at  $t \approx 3 \text{ s}$ . This is in accordance with the primary flow shown in Fig. 3,  
 428 which is only forced in a comparably smaller region, and therefore also results in a  
 429 correspondingly weaker secondary flow.

430

The ratio of the magnetic gradient force to the buoyancy force  $R_{\nabla B}$  for the iron  
 431 cone also shrinks with the deposition time. However, the values are much larger  
 432 than in the two cases considered before. At the final instant considered,  $t = 10 \text{ s}$ ,  
 433  $R_{\text{MHD}} \approx 10$ . This indicates that  $\mathbf{f}_{\nabla B}$  has a much stronger influence on the process

434 than  $\mathbf{f}_L$  and also effectively counteracts the influence of  $\mathbf{f}_g$ , which is in line with the  
 435 discussion of the flow pattern shown in Fig. 4. It should be noted that the region  
 436 where  $\mathbf{f}_g$  acts is extended with the buildup and the advection of the concentration  
 437 boundary layer, while  $\mathbf{f}_{\nabla B}$  is only of importance close to the cone where large field  
 438 gradients are found. This easily explains the decrease in  $R_{\nabla B}$  with the deposition  
 439 time.

### 440 3.2. Flat and sharp cones

441 To enable conclusions to be drawn on how a vertical magnetic field affects the  
 442 growth of surface elevations at the different stages of development, we now include  
 443 flat and steep cones in the investigation. The cone tip angles additionally considered  
 444 are  $30^\circ$  and  $90^\circ$ , with the surface area of the cones remaining constant. More details  
 445 of the cone dimensions are given in Table 3.

446 The shape of the cone can be expected to influence the distribution of the current  
 447 density near the cone and also the magnetic field near the iron cone. We first  
 448 investigate the influence of the current density. For geometrical reasons, steep cones  
 449 are expected to be characterized by a less uniform current density distribution along  
 450 the cone surface compared to flat cones [12]. This is also confirmed by the analytical  
 451 solution of the primary current density distribution along an infinitely extended  
 452 cone as derived in SI. Fig. 8(a) compares the numerically obtained primary current  
 453 density distribution along the surface of the cones with different tip angles studied  
 454 here, exhibiting good qualitative agreement with the analytical solution, as shown  
 455 in Fig. S3 in SI.

456 In order to additionally account for kinetic effects at the electrode, which might  
 457 mitigate the purely geometric effect considered in the primary current density [49,  
 458 50], Fig. 8(b) shows the numerical results of the current density at cones with differ-  
 459 ent tip angles at  $t = 10$  s. In these calculations, the electrode kinetics according to  
 460 Eq. 13 are included, but the electrolyte flow is excluded. Although the inhomogene-  
 461 ity in general is reduced compared to the primary current density shown in Fig. 8(a),  
 462 the numerical results indicate that the steep cone still has the largest value for the  
 463 current density near the tip of the cone. This indicates a stronger Lorentz force  
 464 effect for steeper cones.

465 A variation in the shape of the iron cones also affects the distribution of the  
 466 magnetic field nearby. Fig. 9 shows the magnitudes of  $B$  and  $B\nabla B$  along a nearby  
 467 surface-parallel line for cones of different tip angles. In the vicinity of the cone tip,  
 468 as already mentioned above, the sharp edge of the magnetized surface generally  
 469 leads to a high magnetic flux density [40]. This implies that when the cone becomes  
 470 sharper, a stronger stray field and correspondingly a stronger field gradient is found  
 471 near its tip. However, for steeper cones, the cone surface grows more parallel to the  
 472 external vertical field. This reduces the demagnetization of the Fe cones, which also  
 473 reduces the stray field and thus the magnetic gradient near the cones. For more

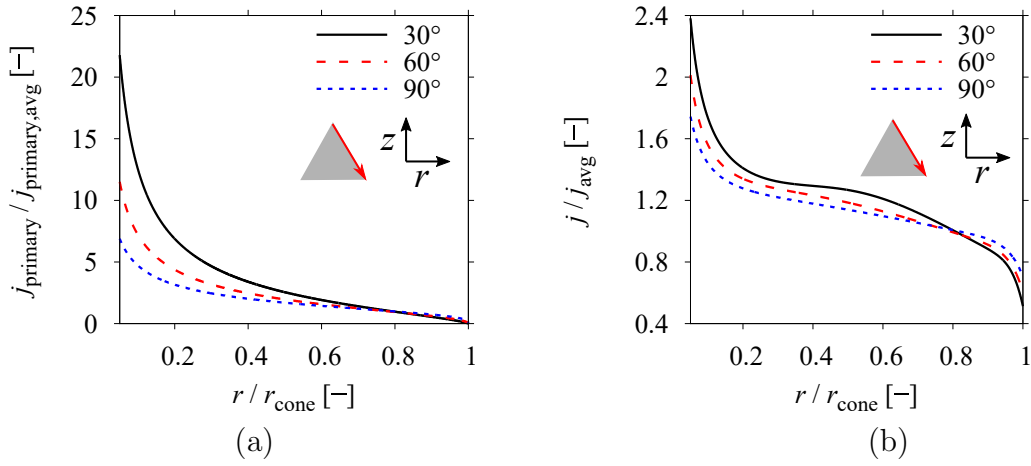


Figure 8: (a) Normalized primary current density and (b) normalized current density (No magnetic field, no convection) at cones of different tip angles  $\alpha_{\text{tip}}$  after 10 s of deposition.  $j_{\text{cathode,avg}} = 16 \text{ mA/cm}^2$ . The horizontal axis shows the radial surface coordinate normalized by the cone radius  $r_{\text{cone}}$ .

474 details on the magnetization of ferromagnetic surfaces in external magnetic fields,  
 475 we refer to [40]. Due to the two opposite effects mentioned, the intermediate cone tip  
 476 angle of  $60^\circ$  presented in Fig. 9 yields the strongest amplitudes of  $B$  and  $B\nabla B$  near  
 477 the tip. The strongest influence of the magnetic gradient force on the deposition  
 might further be expected to be found at intermediate cone tip angles.

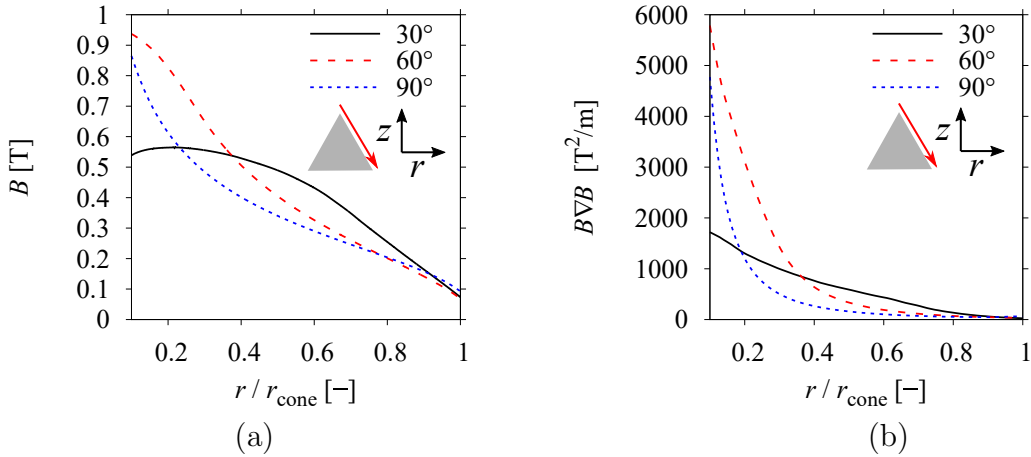


Figure 9: Magnitudes of (a) the magnetic flux density  $B$  and (b) the magnetic gradient term  $B\nabla B$  along a monitoring line parallel and near (distance  $35 \mu\text{m}$ ) to the slanted surface of Fe cones of different tip angles.  $B_0 = 200 \text{ mT}$ . The horizontal axis shows the radial surface coordinate normalized by the cone radius  $r_{\text{cone}}$ .

478

479 Eventually, the simulation of the deposition process at copper and iron cones  
 480 of different shapes, Fig. 10, shows the distribution of the copper ion species and  
 481 the meridional velocity vectors obtained after a deposition time of 10 s. For the  
 482 copper cones, the downward secondary flow driven by  $\mathbf{f}_{\mathbf{L}}$  is strongest for the steep  
 483 cone of  $\alpha_{\text{tip}} = 30^\circ$  and weakest for the flat cone of  $\alpha_{\text{tip}} = 90^\circ$ . As the magnetic field  
 484 remains unchanged, this is in line with the behavior of the current densities shown in  
 485 Fig. 8. Furthermore, although not shown in detail, a larger region with horizontal  
 486 components of the current density exists near steeper cones, as the vectors must

487 become normal to the cone surface. All this compensates for the closer proximity  
 488 of the cone surface to the symmetry axis, which reduces the azimuthal momentum  
 489 delivered by  $\mathbf{f}_L$ . For the steep cone, the concentration boundary layer rising from  
 490 below is forced to separate from the cone surface slightly below the tip due to the  
 491 strong downward flow, locally reducing the thickness of the boundary layer. The  
 492 flatter the cone becomes, the weaker the downward flow caused by  $\mathbf{f}_L$ , while the  
 493 concentration boundary layer passes the cone tip and continues to rise freely. This  
 494 leads to a thicker concentration boundary layer near the tip of the cone, as observed  
 495 also experimentally for an intermediate tip angle in [1]. The plume-like shape of the  
 496 tip of the separated concentration boundary layer is similar to the behavior of the  
 temperature in free thermal convection [51].

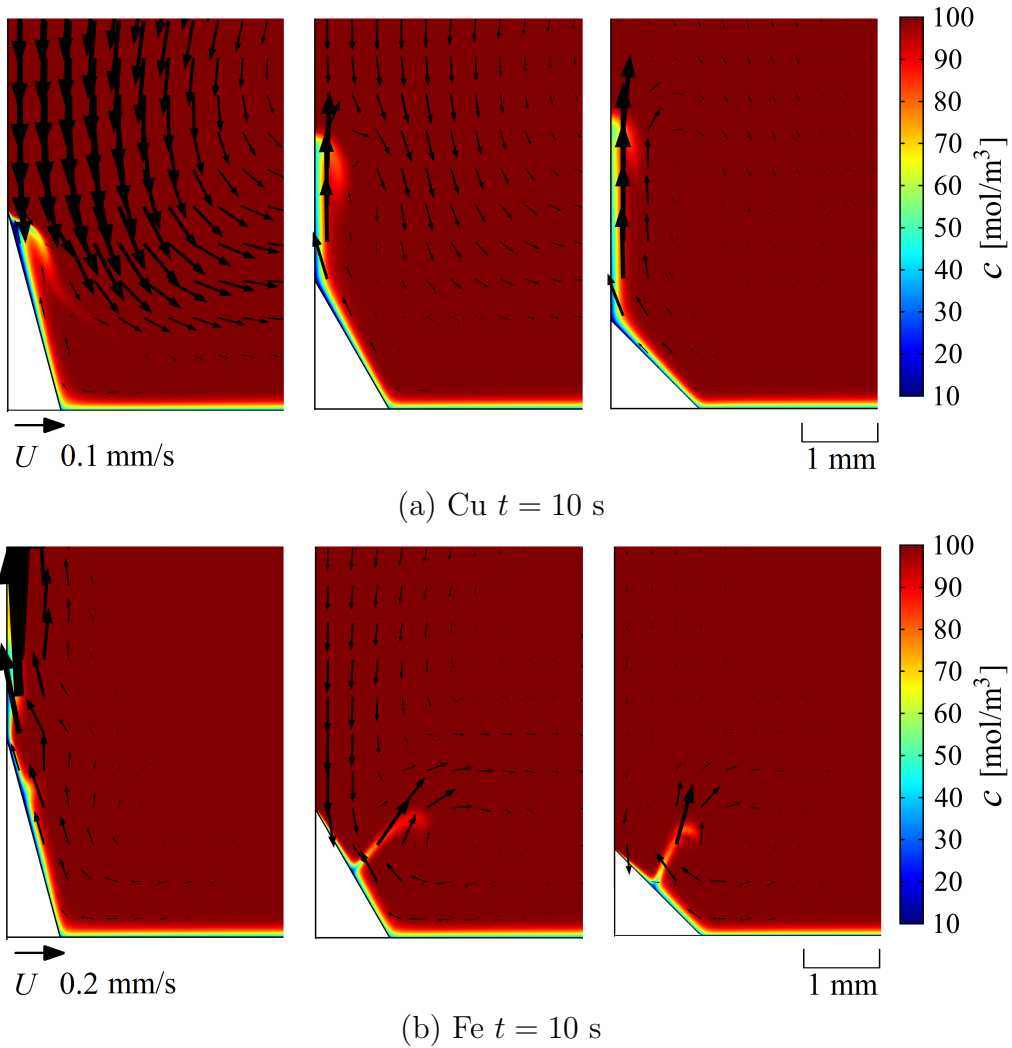


Figure 10: Color surface of the concentration near (a) Cu and (b) Fe cones after 10 s deposition time ( $j_{\text{cathode,avg}} = 16$  mA/cm<sup>2</sup>,  $B_0 = 200$  mT). Black arrows represent the meridional velocity vectors. Cone tip angles from left to right: 30°, 60°, 90°.

497

498 For the steep iron cone, unlike the case of copper, the concentration boundary  
 499 layer quickly rises vertically; its tip has already crossed the upper boundary of  
 500 the region shown. This can be understood from Fig. 3, which shows a smaller  
 501 region of azimuthal flow driven by  $\mathbf{f}_L$  compared to a copper cone. This results in

502 a correspondingly weaker secondary downward flow. The magnetic gradient force is  
 503 also weakest for steep cones, as can be inferred from Fig. 9. Thus, the magnetic forces  
 504 here are not strong enough to generate a downward flow. However, the interplay  
 505 with buoyancy results in slight variations in the thickness of the rising boundary  
 506 layer. For flatter iron cones, a downward flow towards the cone can be observed,  
 507 which is stronger at  $\alpha_{\text{tip}} = 60^\circ$  compared to  $\alpha_{\text{tip}} = 90^\circ$ , in full agreement with the  
 508 discussion on the magnetic gradient term shown in Fig. 9. Compared to the copper  
 509 cones discussed above, it can be concluded that this flow is mainly forced by  $\mathbf{f}_{\nabla\mathbf{B}}$ . As  
 510 already discussed above, for  $\alpha_{\text{tip}} = 60^\circ$  the concentration boundary layer separates  
 511 from the cone at half its height. This is also observed in the case of the flat cone,  
 512 where the weaker influence of  $\mathbf{f}_{\nabla\mathbf{B}}$  is balanced by the comparably weaker influence  
 513 of  $\mathbf{f}_{\mathbf{g}}$ .

514 In order to evaluate the cumulative influence of the magnetic forces on the de-  
 515 position, in Fig. 11 we compare the deposit thickness obtained after a deposition  
 516 period of 10 s at the copper and iron cones of different shapes. In the absence of a  
 517 magnetic field, as discussed above (see Fig. 8), at steep cones the natural support for  
 518 further cone growth is most pronounced. When a magnetic field is applied, at steep  
 519 cones the Lorentz force considerably enhances growth near the tip of the copper  
 520 cone, whereas at the iron cone the support of the magnetic field for cone growth is  
 521 comparably small. The intermediate tip angle of  $60^\circ$  was already discussed above,  
 522 see Fig. 6. For the flat cone, the situation is opposite to the steep cone. The in-  
 523 fluence of  $\mathbf{f}_{\mathbf{L}}$  at the copper cone is negligible, whereas a profound enhancement of  
 cone growth at the iron cone can be reported, mainly due to  $\mathbf{f}_{\nabla\mathbf{B}}$ .

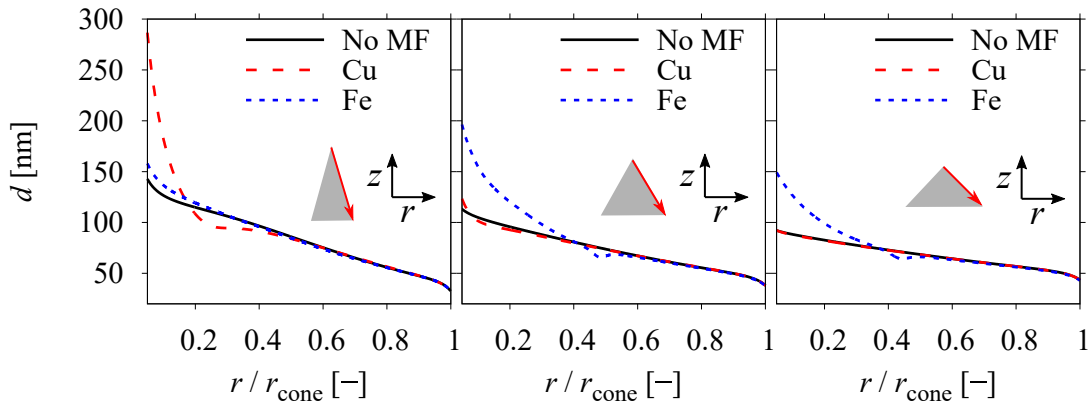


Figure 11: Deposit thickness on cones of tip angles  $30^\circ$ (left),  $60^\circ$ (middle) and  $90^\circ$ (right) after 10 s of deposition for the case without a magnetic field (no MF) and for Cu and Fe cones with a magnetic field ( $j_{\text{cathode,avg}} = 16 \text{ mA/cm}^2$ ,  $B_0 = 200 \text{ mT}$ ). The horizontal axis shows the radial surface coordinate normalized by the cone radius  $r_{\text{cone}}$ . The case of  $60^\circ$  is reprinted from Fig. 6 for comparison.

524

525 Table 4 summarizes the relative enhancement of the deposit thickness at the  
 526 tip of the Cu and Fe cones compared to the case without a magnetic field after a  
 527 deposition time of 10 s. It can be concluded that cone growth at diamagnetic cones  
 528 supported by the action of  $\mathbf{f}_{\mathbf{L}}$  works best for cones of a sharp shape. However, as

529 the support at flat cones seems to be negligible, the benefit of magnetic fields for  
 530 the further development of early flat surface elevations seems rather limited.

531 For ferromagnetic cones, a promising enhancement of the deposit thickness was  
 532 found for all the cone shapes studied here, mainly caused by the magnetic gradient  
 533 force. The supporting effect was found to be the greatest with intermediate tip  
 534 angles and to be moderate only in the case of steep cones. As can be seen from  
 535 Fig. 11, when starting from a flat surface elevation, cone growth accelerates during  
 536 deposition as the cone tip angle becomes smaller. The cone continues to grow  
 537 and to become sharper. However, as soon as the optimum intermediate tip angle  
 538 associated with the strongest support from the magnetic gradient force is passed,  
 this sharpening slows down.

Table 4: Enhancement of the deposit thickness at the Cu and Fe cone tips compared to the case without a magnetic field after 10 s deposition time ( $\alpha_{\text{tip}} = 30^\circ, 60^\circ, 90^\circ$ ,  $j_{\text{cathode,avg}} = 16 \text{ mA/cm}^2$ ,  $B_0 = 200 \text{ mT}$ ).

Cone tip angle	Cu	Fe
$30^\circ$	+93%	+10%
$60^\circ$	+9%	+73%
$90^\circ$	$\approx 0$	+62%

539

### 540 3.3. Influence of neighboring cones

541 Depending on the distance between adjacent cones, the flow forced at each single  
 542 cone may be affected by the flow originating from its neighbors. Thus, mass transfer  
 543 might also change. We therefore now extend our investigation to take into consider-  
 544 ation the influence of neighboring cones. We first consider regular arrangements of  
 545 cones on a quadratic lattice as shown in Fig. 2(c). These investigations correspond  
 546 to Step 2 of the simulation methodology mentioned earlier.

547 As a result of the 3D simulations performed, Fig. 12 shows the horizontal com-  
 548 ponents of the electrolyte velocity in a horizontal plane above the cathode touching  
 549 the tips of copper cones. A square with four neighboring cones is shown, and the  
 550 distance between the cone centers is varied from 5 to 1.5 cone diameters  $d_{\text{cone}}$  (see  
 551 Fig. 2). At the large cone distance, a strong azimuthal flow in an anticlockwise  
 552 direction is clearly visible, driven by  $\mathbf{f}_{\mathbf{L}}$ . As known from the single cone studies,  
 553 this flow extends in a radial direction far beyond the cone radius (see Fig. 3). In the  
 554 outer region close to half the cone distance, the neighbor influence becomes visible  
 555 as a deformation of the circular shape of the azimuthal velocity contours towards a  
 556 square. At half of the distance between the cones, the horizontal velocity is consid-  
 557 erably reduced, as the two azimuthal flows are in opposite directions and hamper  
 558 each other. When the distance between the cones is reduced, this damping influence  
 559 increases, as seen from the lower amplitude of the azimuthal flow. At the same  
 560 time, small clockwise-rotating vortices are formed at the four vertical edges of the

561 computational domain (most clearly visible in the center of the squares shown in  
 562 Fig. 12), the amplitude of which is weak in comparison to the primary flow.

563 Fig. 13 shows the corresponding vertical velocity components in the vertical  
 564 plane across the center of the copper cone. Because of symmetry, the results in  $x$   
 565 or  $y$  direction are identical. As the primary rotational flow is slowed down when  
 566 the cones grow closer to each other, the secondary downward flow forced by  $\mathbf{f}_L$  also  
 567 gets correspondingly weaker and has nearly disappeared at the small cone distance  
 568 of  $1.5 d_{\text{cone}}$ . Thus, the support of cone growth in a magnetic field is weakened as the  
 area density of the cones grows.

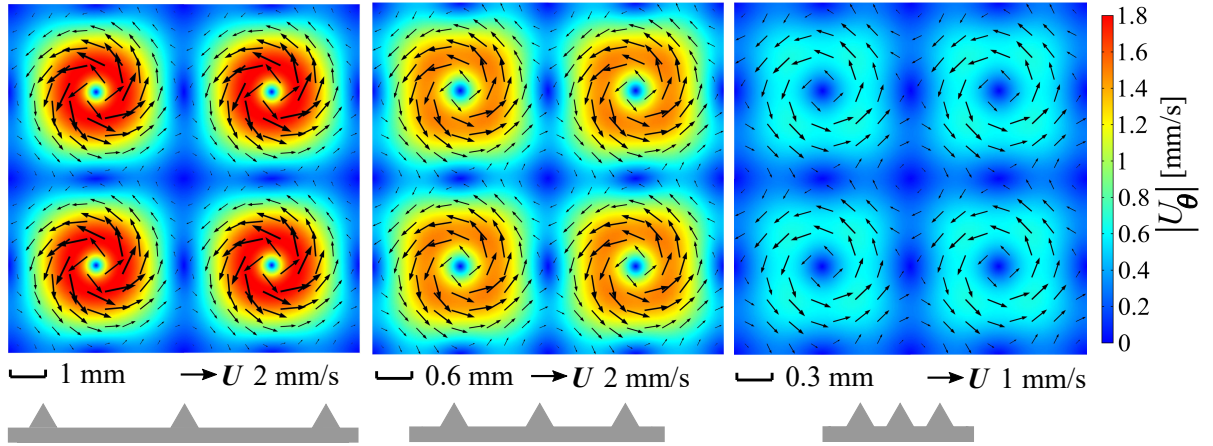


Figure 12: Horizontal velocity in a horizontal plane touching the tips of the neighboring copper cones obtained from 3D simulations after a deposition time of 5 s ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 8$  mA/cm<sup>2</sup>,  $B_0 = 400$  mT). Black arrows of the horizontal velocity vectors and color contours of the azimuthal velocity component. The cone distance in units of  $d_{\text{cone}}$  shrinks from left to right (5, 3, 1.5). Note that the scale of length and of the velocity vectors changes from left to right.

569

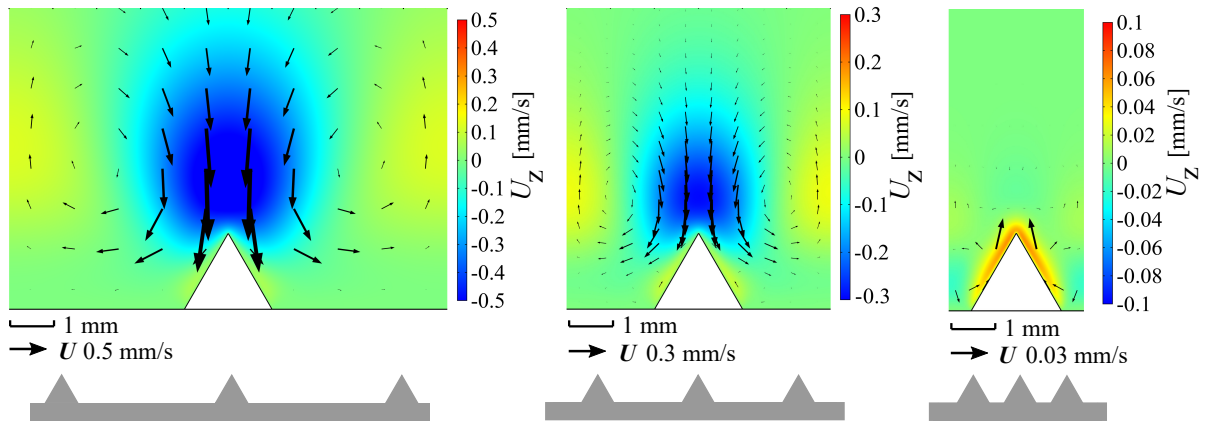


Figure 13: Vertical velocity on the vertical plane across the center of the copper cone in  $x$  direction obtained from 3D simulations after a deposition time of 5 s ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 8$  mA/cm<sup>2</sup>,  $B_0 = 400$  mT). The cone distance in units of  $d_{\text{cone}}$  shrinks from left to right (5, 3, 1.5). Black arrows represent the velocity vectors, the scale of which changes from left to right.

570 It should be mentioned that the computational effort for these 3D simulations  
 571 is great and would be even greater for the iron cones, where steep gradients in the  
 572 magnetic field near the surface of the cones additionally need to be accurately re-  
 573 solved. A validation of the axisymmetric 2D approach denoted as Step 3 in Section



574 2.1 could allow the computational effort for these simulations to be reduced consid-  
575 erably. This is motivated by the persistence of strong axisymmetry at a shrinking  
576 cone distance, as shown in Fig. 12. We therefore next present a comparison of results  
577 obtained by the 3D method and by the axisymmetric 2D approach for Cu cones.  
578 Fig. 14(a) shows the magnitude of the maximum azimuthal velocity of the primary  
579 flow versus the cone distance after a deposition time of 5 s. The results of the 3D  
580 and 2D approaches for the Cu case are close and follow the trend mentioned above  
581 of the azimuthal rotational flow becoming weaker if the cone distance is reduced.  
582 Fig. 14(b) shows the vertical velocity measured slightly above the cone tip. Again,  
583 both 3D and 2D results in the case of Cu are close and show that the downward  
584 flow velocity weakens. In both cases, the 2D axisymmetric results slightly overstate  
585 the damping influence compared to the 3D results, which is reasonable, as immedi-  
586 ately neighboring cones are assumed to be found at every angular position compared  
587 to only four immediately neighboring cones in the 3D case. Nevertheless, the ax-  
588 isymmetric 2D approach proves to be an accurate and effective means of studying  
589 the neighbor influence. The intrinsic slight overestimation of the neighbor influence  
590 allows upper boundaries for the damping neighbor effect to be found quickly. All  
591 results presented in the following, including the cases of the iron cones, are therefore  
obtained by 2D simulations.

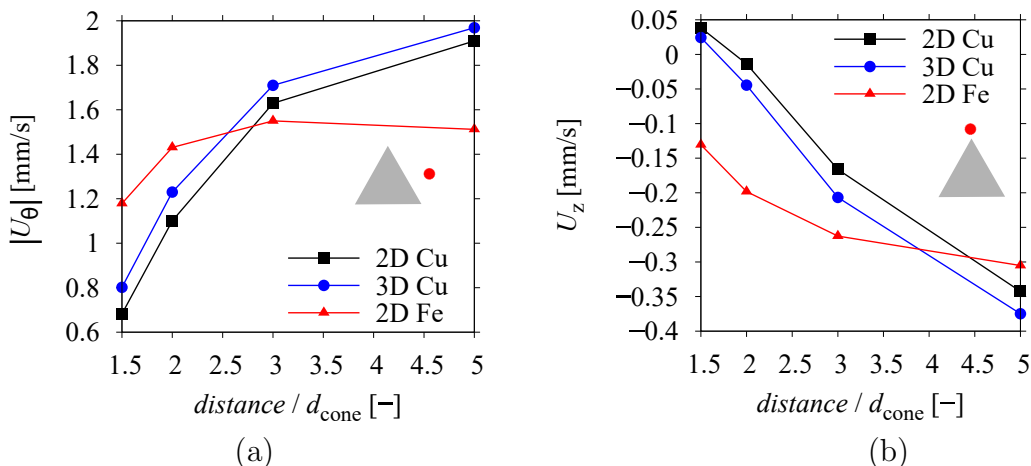


Figure 14: (a) Magnitude of the maximal azimuthal velocity,  $|U_\theta|$ , and (b) the vertical velocity  $U_z$  at 0.3 mm above the cone tip versus cone distance for Cu (2D and 3D results) and Fe cones (2D results) after 5 s of deposition ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 8 \text{ mA/cm}^2$ ,  $B_0 = 400 \text{ mT}$ ).

592

593 For the iron cones, unlike the copper cones, varying the distance between the  
594 cones can change their magnetization and thus the magnetic field. Fig. 15 shows  
595 the magnitudes of  $B$  and  $B\nabla B$  near the cone surface for different cone distances.  
596 When the neighboring cones grow closer, the magnetic field near a magnetized Fe  
597 cone becomes slightly weaker. Regarding the magnetic field gradient term, reducing  
598 the distance to the neighbor cones has a small influence near the lower half of the  
599 iron cone only.

600

As shown in Fig. 14, shrinking the cone distance has a much weaker effect on the

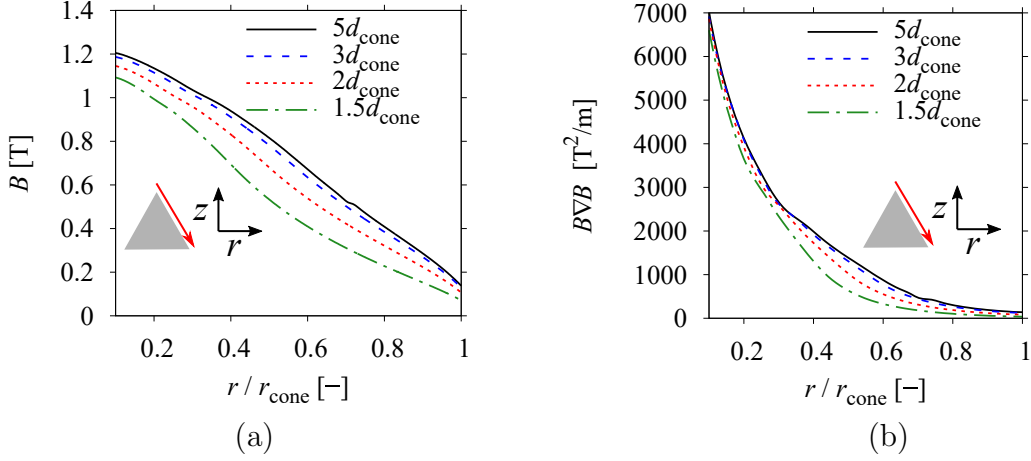


Figure 15: Magnitudes of (a) the magnetic flux density,  $B$ , and (b) the magnetic gradient term,  $B\nabla B$ , along a monitoring line parallel to the slanted cone surface (distance to the cone surface:  $35\ \mu\text{m}$ ) for different distances between the Fe cones ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 8\ \text{mA}/\text{cm}^2$ ,  $B_0 = 400\ \text{mT}$ ). The horizontal axis shows the radial surface coordinate normalized by the cone radius  $r_{\text{cone}}$ .

601 electrolyte flow near the iron cones compared to the copper cones. The maximum  
 602 azimuthal velocity shown on the left (a) remains nearly constant and eventually de-  
 603 creases only slightly towards a distance of  $1.5\ d_{\text{cone}}$ . The comparably weak neighbor  
 604 effects on the azimuthal flow are related to the bending of the magnetic field near the  
 605 iron cones. More details are given in SI. The vertical velocity shown on the right (b)  
 606 and depicted slightly above the cone tip, contrary to the Cu cones, remains negative  
 607 even at the shortest distance of  $1.5\ d_{\text{cone}}$  shown. As the cone distance shrinks, this  
 608 downward flow is also weakened due to the continuity of the flow, as the vertical  
 609 backflow in the narrow gap between the cones is in the opposite direction. But the  
 610 slowing of this flow is moderate only. The obvious reason is that the downward flow  
 611 caused by  $\mathbf{f}_{\nabla B}$  is driven near the cones. This is unlike the downward flow caused  
 612 by  $\mathbf{f}_{\mathbf{L}}$ , which is a result of the primary azimuthal flow driven in a radially extended  
 613 region. Thus, the supporting influence of  $\mathbf{f}_{\nabla B}$  for cone growth can be expected to  
 614 be less affected by neighboring cones compared to  $\mathbf{f}_{\mathbf{L}}$ .

615 Fig. 16(a) shows the concentration and meridional flow for the Cu case at a  
 616 later deposition time (13 s), at which the downward secondary flow caused by  $\mathbf{f}_{\mathbf{L}}$  is  
 617 only visible at the largest cone distance. As the distance between the cones shrinks  
 618 and the secondary flow of the Lorentz force becomes weaker, the buoyant upward  
 619 convection of the concentration boundary layer is enhanced. The only exception is  
 620 that, as the cone distance decreases from  $2\ d_{\text{cone}}$  to  $1.5\ d_{\text{cone}}$ , the buoyant flow seems  
 621 to be slightly weaker again, as seen from the height of the buoyancy plume. This  
 622 might be due to stronger damping between the upward buoyant flow and the down-  
 623 ward backflow, as the radial distance between these two flow regions also shrinks  
 624 with the cone distance.

625 In the case of the iron cones, as shown in Fig. 16(b), unlike the Cu cones, the  
 626 downward flow resulting from the two magnetic forces seems to be only slightly  
 627 weakened as the cone distance shrinks. Therefore, support for cone growth by the

628 magnetic field can be expected in all cases. The weakening of the downward flow  
 629 results in a slight increase in the height at which the concentration boundary layer  
 630 leaves the cone, as discussed above in the case of single iron cones. In all cases,  
 631 the concentration boundary layer at the Fe cones exhibits further periodic thickness  
 632 variations along the cone at a length scale much smaller than the cone diameter.  
 633 These are mainly caused by the action of the magnetic gradient force  $\mathbf{f}_{\nabla B}$ . The  
 634 position of the departing jet of depleted electrolyte can also be understood as the  
 most unstable location of the boundary layer [38, 52].

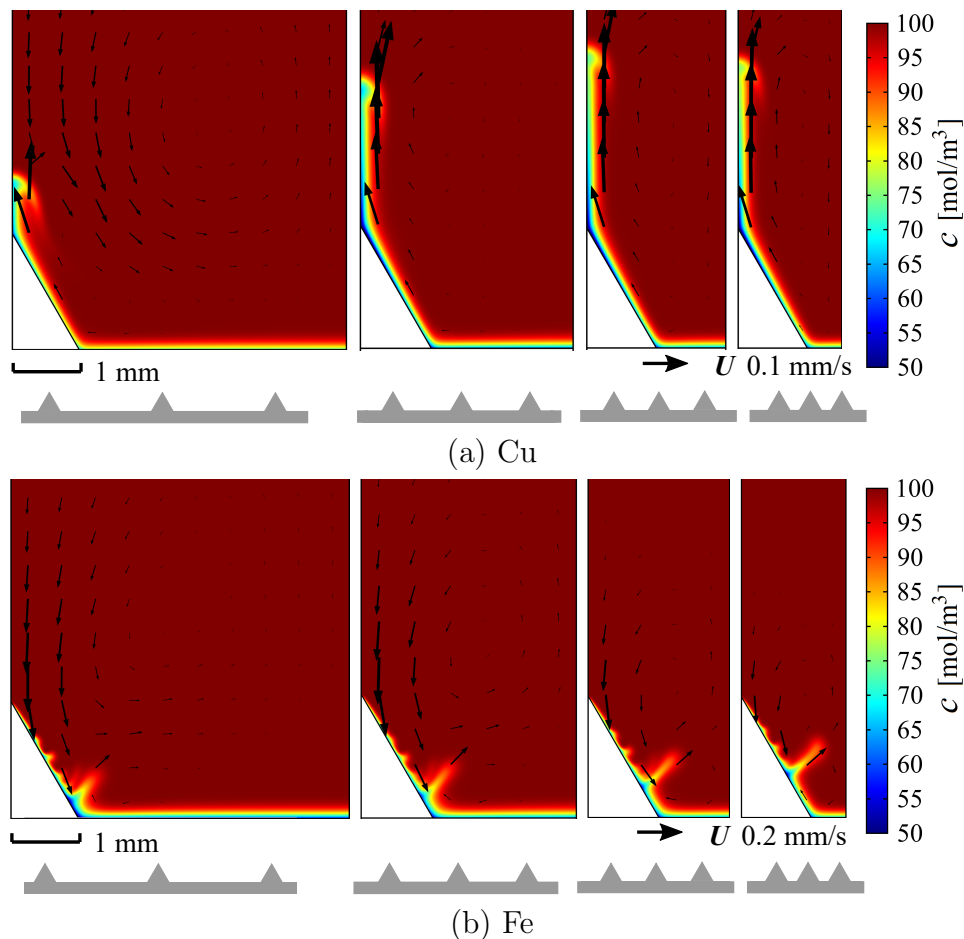


Figure 16: Species concentration (color surface) and meridional velocity vectors (black arrows) for (a) Cu and (b) Fe cones at different distances after 13 s of deposition. ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 8 \text{ mA/cm}^2$ ,  $B_0 = 400 \text{ mT}$ ). The cone distance in unit of  $d_{\text{cone}}$  shrinks from left to right (5, 3, 2, 1.5). Note that the scales of the velocity vectors for Cu and Fe cones are different.

635

636 Finally, Fig. 17 shows the deposit thickness obtained for the smallest cone distance  
 637 of  $1.5 d_{\text{cone}}$  investigated. A longer deposition time of 50 s is also considered.  
 638 As can be seen, for the Cu cones, the structuring effect due to  $\mathbf{f}_{\mathbf{L}}$  is negligible when  
 639 compared to the case without a magnetic field, which is in accordance with the  
 640 buoyancy-dominated flow pattern shown in Fig. 16(a). For the iron cones, however,  
 641 the support for cone growth by the magnetic field, i.e. mainly by  $\mathbf{f}_{\nabla B}$ , is clearly  
 642 visible.

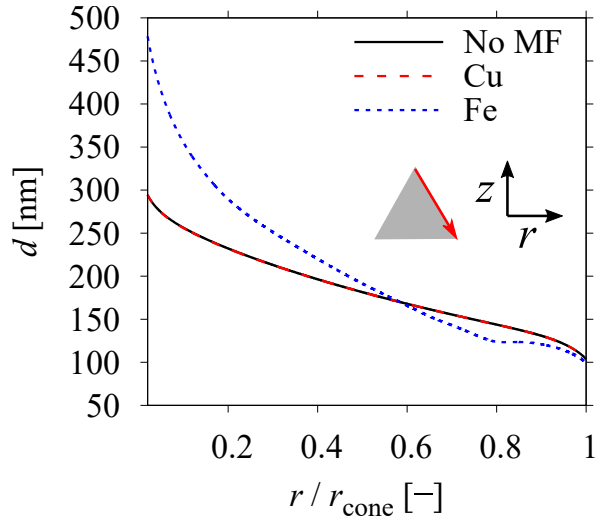


Figure 17: Deposit thickness along the cone surface for the case without a magnetic field (No MF) and for Cu and Fe cones in a vertical magnetic field after 50 s of deposition ( $\alpha_{\text{tip}} = 60^\circ$ ,  $j_{\text{cathode,avg}} = 8 \text{ mA/cm}^2$ ,  $B_0 = 400 \text{ mT}$ ). The distance to neighboring cones is  $1.5d_{\text{cone}}$ , the horizontal axis shows the radial surface coordinate normalized by the cone radius  $r_{\text{cone}}$ .

#### 643 4. Conclusions

644 The analytical and numerical results of this work offer an insight into the basic  
 645 effects of a vertical magnetic field on electrodeposition at conically shaped metal  
 646 electrodes. The focus is on ferromagnetic conical structures of mm size. We show  
 647 that cone growth can be supported by the flow driven by the Lorentz force and  
 648 the magnetic gradient force that enriches the electrolyte near the cone, and thus  
 649 enhances the local mass transfer.

650 As the cathode is assumed to be placed at the bottom of the electrochemical  
 651 cell, the beneficial magnetic effects are counteracted by solutal buoyancy arising  
 652 from the electrode reaction. The Lorentz force is surpassed by the buoyancy force  
 653 after the first few seconds of the deposition. In comparison, the magnetic gradient  
 654 force enabled by the magnetization of the ferromagnetic cones provides stronger  
 655 support for cone growth, thereby often dominating over buoyancy. In general, the  
 656 flow is caused by the rotational parts of both magnetic gradient force and buoyancy  
 657 force.

658 We studied cones with different tip angles and found that the sharpest cone  
 659 yields the strongest Lorentz force, while an intermediate cone tip angle generates  
 660 the highest magnetic gradient force. As the evolution of the conical structures  
 661 usually develops from flat surface elevations, it could be anticipated that the growth  
 662 of ferromagnetic cones may be slow at the beginning, followed by an acceleration  
 663 of the growth speed until an optimum shape is approached with respect to the  
 664 supporting effect. Later on, growth will continue at a lower speed.

665 When the neighboring cones come closer to each other, the azimuthal flow caused  
 666 by the Lorentz force is strongly damped. In comparison, the meridional flow caused  
 667 by the magnetic gradient force is less affected, as it is driven in the close vicinity of

668 the cone surface.

669 Our results demonstrate the superiority of the magnetic gradient force in terms  
670 of supporting the structured electrodeposition in a magnetic field. We expect this  
671 superiority to enhance further when extending the investigation towards the micro-  
672 and nanometer scale, where larger field gradients are to be expected. This may en-  
673 courage further research on magnetic field assisted electrodeposition as a simple and  
674 efficient method for synthesizing micro- and nano-structured ferromagnetic surfaces.

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