

1 Flotation of alumina on the surface of 2 the electrolyte in an aluminum 3 electrolysis cell

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22 **Abstract**

23 A model of flotation was developed and applied to alumina in the aluminum electrolysis cell.
24 The conditions of flotation for alumina on the cryolitic bath surface and bath-metal interface
25 were determined for disc and sphere geometries. The contact angle between alumina and
26 cryolitic bath, which had not been found in the literature, was measured and it was found to be
27 around 30°. Experiments with compressed alumina discs on the cryolitic bath surface were
28 conducted, and the results were compared to the model. The experiments showed how
29 impurities on the bath surface influence the flotation; and how a slight asymmetry in the system
30 may accelerate sinking.

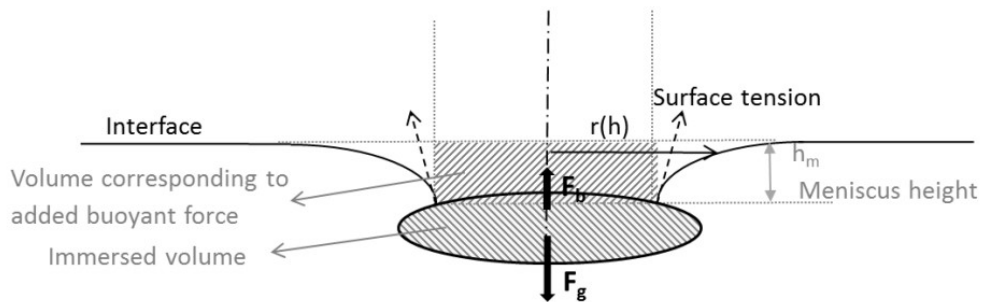
31 **Introduction**

32 To produce aluminum, alumina powder (Al_2O_3) needs to be dissolved in molten cryolitic bath.
33 Certain behaviors of smelter grade alumina are well known in the industry, such as its tendency
34 to stay afloat on the surface of the electrolyte after the injection, as well as its potential to form
35 aggregates - frequently called "rafts". Alumina aggregates can also sink below the liquid
36 aluminum at the bottom of the cell, forming deposits (sludge). These phenomena are noted by
37 several researchers and they form part of the general knowledge of the industry, although
38 several important details have not been analyzed in depth. As the conditions for dissolution are
39 considerably different inside the agitated bath than on its surface, the problem of raft flotation
40 deserves more attention. The sludge formation below the metal pad attracted more interest,
41 because the presence of alumina on the carbon cathode influences the distribution of the
42 current and may cause operational problems. The aim of this work is to investigate the
43 conditions of flotation of alumina on the cryolitic bath surface and on bath-metal interface, and
44 to estimate the flotation limit in static conditions.

45

46 Flotation

47 According to Newton's first law, an object at rest will stay at rest as long as the sum of all forces
48 acting upon it is zero. It is known since Archimedes that a floating object is subjected to a
49 buoyant force, equivalent to the weight of the displaced fluid. The equilibrium of the
50 gravitational and the buoyant forces are sufficient to determine the floatability and immersion
51 of a large body, such as a ship, but the surface tension plays an important role in the flotation of
52 small objects (Figure 1).



53

54

55 Figure 1: Forces acting on a floating axisymmetric object

56

57 The surface tension may contribute to the flotation in two ways. The vertical component of the
58 surface tension acting along the triple line is influenced by the so-called contact angle of the
59 liquid surface at the triple line. The surface tension can aid the flotation but it can hinder it as
60 well, depending on the wetting characteristics of the liquid-solid system. The meniscus around a
61 floating object is also the result of the surface tension and it influences the hydrostatic pressure,
62 therefore the buoyant force acting on the object.

63 Meniscus height

64 The surface tension is the result of the cohesive forces between the molecules of a liquid.
65 Molecules on the surface lack neighbors on one side, so the cohesive forces act on the liquid
66 side only and pull the surface towards the bulk of the liquid. It leads to a curved surface, also
67 called meniscus. The connection between the curvature of the meniscus and the pressure
68 difference across the surface or interface is described by the Young-Laplace equation (Eq. 1).

$$\Delta p = \gamma \left(\frac{1}{R_x} + \frac{1}{R_y} \right) = \gamma 2K \quad (1)$$

69

70

71 Δp : Laplace pressure

72 γ : surface tension

73 R_x, R_y radius of curvature in two perpendicular axes in the tangent plane to the surface.

74 K : mean surface curvature

75 The inclusion of the meniscus height in a flotation model can be done in various ways. The
76 simplest solution is to neglect the meniscus height altogether, and consider the buoyant force
77 corresponding to the volume of the object below the triple line [1] or below the undisturbed
78 surface [2]. It is a pragmatic solution, which results in a negligible inaccuracy for the flotation of
79 particles significantly smaller than the capillary length (Eq. (7)) of the interface, as is the case
80 with the flotation of individual smelter grade alumina particles on the surface of the electrolyte.
81 Solheim applied the meniscus height calculated beside a plane wall to determine the flotation
82 limit of disc-shaped alumina agglomerates on the bath-metal interface [3]. The meniscus height
83 around a cylinder approaches that around a plane wall as the radius increases, which makes this
84 estimation appropriate for large objects. The most precise method would be to solve the Young-
85 Laplace equation. Singh used direct numerical simulation of the water-air interface to determine
86 the behavior of floating particles, and as he pointed out, the required computational capacity
87 increases unfeasibly when there are several objects on the surface [4].

88 In this work the equation describing liquid surface around axisymmetric objects [5] was solved
89 numerically to obtain the meniscus height Eq. (2):

$$K = \frac{r''}{(1 + r'^2)^{3/2}} - \frac{r'}{(b + r)(1 + r'^2)^{1/2}} \quad (2)$$

90

91 Where:

92 b: radius of axisymmetric object at the triple line

93 $r=r(h)$: interface profile, (see Figure 1)

94 r' , r'' : first and second derivatives of $r(h)$

95 h: meniscus height/depth, axial (vertical) coordinate

96 From Eq. 1, the surface curvature can be expressed as a function of the capillary pressure, which
97 is proportional to the meniscus height (-h). Matlab ordinary differential equation solvers can
98 only solve first order equations; therefore the second order equation was rewritten as an
99 equivalent system of first order equations. The meniscus height was in question; an initial value
100 was specified, then trial and error method was used to obtain the final result.

101 Angle of interface at triple line

102 The angle of the interface at the triple line is necessary to find the vertical component of the
103 surface tension, and also as a boundary condition for the Young-Laplace equation to determine
104 the meniscus height. For smooth, homogenous surfaces, the Young-Dupré equation shows the
105 connection between the interfacial energies and the equilibrium contact angle. If the floating
106 object has a smooth surface, the angle of the object at the triple line and the contact angle
107 determine the angle of the liquid surface Eq. (3)

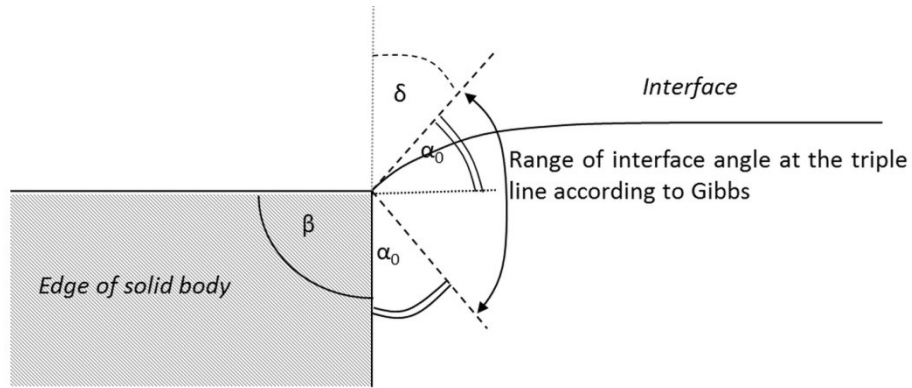
$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cos \alpha \quad (3)$$

108 The contact angle (α) has a significant influence on the flotation. A large contact angle will
109 permit the floating object to descend deeper below the line of the undisturbed surface without
110 sinking than an object wetted by the liquid could. But that is not to say flotation of an object
111 denser than the liquid is not possible even if the contact angle defined by the Young-Dupre
112 equation would reach 0° , as the shape and surface quality of the solid would also influence the
113 angle of the interface at the contact line (δ) (Figure 2: Illustration for Gibbs extension to Young-
114 Dupré law.

115 In the mathematical model, two different geometries were considered: spheres and cylinders
116 (round disks). The spherical objects were considered smooth, but the effect of roughness can be
117 investigated by increasing the apparent contact angle in the model. In case of circular disks, the
118 angle of the interface at the edge has a degree of freedom as specified by Gibbs [2] Eq. (4).

$$\alpha_0 < \alpha < 180 - \beta + \alpha_0 \quad (4)$$

119 Where α_0 is the static equilibrium contact angle and β is the angle of the corner of the solid body
120 as shown in Figure 2.



121

122

123

Figure 2: Illustration for Gibbs extension to Young-Dupré law

124

125 On rough or heterogeneous surfaces, the Young equation is only locally applicable, although the
 126 Wenzel and the Cassie-Baxter equations offer estimations for the apparent contact angle (α) for
 127 different wetted states. [5]

128

129 To determine the angle of the interface at the contact line, both the shape of the object and the
 130 contact angle should be known, however it is often not the case. Maru's approximation for
 131 maximal radius of a floating spherical object is independent of the contact angle. His equation
 132 has been used to calculate the flotation limit of solid alumina agglomerate on the bath-metal
 133 interface. As the result, 7.5 mm was calculated as the critical diameter [6].

134 Flotation in mineral industry

135 Particle flotation has been used in the mineral industry for more than a hundred years to
 136 separate valuable ores from the waste. The ores are crushed, and then mixed in with water and
 137 possibly other additives. Air is fed into the slurry and the rising bubbles collect and transport
 138 certain minerals to the surface, as particles get attached to the interface of the bubbles [7].
 139 Most researchers in this field have a more practical than theoretical approach, focusing not on
 140 the possibility but the probability of flotation, the particle retention. Flotation models can be
 141 found, albeit sometimes crude and the bulk of the works is empiric [8] [9] [10]. Although there
 142 are unarguably differences, it is worth pointing out that the anode gas forming in the electrolysis
 143 cells also creates a current of bubbles in the electrolyte. This parallel might become even more
 144 significant in the future with inert anode technology, as they work with saturated bath that
 145 would promote the presence of undissolved alumina.

146 Flotation of alumina in the cryolitic bath, along the bath-metal interface

147 Generally, the analysis of the flotation conditions on the bath surface has not generated much
148 interest. Walker measured the density of alumina rafts and found that they can float even when
149 their density exceeds the density of the cryolitic bath [11]. The flotation of carbon particles on
150 the bath, and their interference with the measurement of the surface tension, noted by
151 Kucharic [12] is worth mentioning as the same issue was encountered by the authors of this
152 paper, and industrial cells are contaminated with carbon dust even more than experimental
153 setups.

154 The possibility of flotation of alumina agglomerates on the bath-metal interface is of more direct
155 importance to the industry. A flotation model of disc-shaped agglomerates has been presented
156 by Solheim [3], and a simple estimation for the flotation limit of spherical agglomerates by
157 Thonstad [6]. Both of them focused mainly on the possibility of an alumina particle layer on the
158 interface. They theorize that the alumina layer on the interface impedes mass transfer of
159 aluminum, therefore decreases the re-oxidation of the metal by the anode gas and increases
160 current efficiency. Solheim proved the possibility of alumina and cryolite precipitation on the
161 interface through theoretical investigation of bath chemistry [13], though he later pointed out
162 that Marangoni convection might clear the interface of those particles [3].

163 Properties of alumina-bath system, input data for flotation model

164 The values of density, interfacial tension and contact angle are necessary for the calculation of
165 forces on the interface. The density of the electrolytic bath depends on its temperature and
166 composition. To maintain good separation between the bath and liquid aluminum, the latter
167 having a density of 2.3 g/cm³, the bath density is usually kept around 2.1 g/cm³ or below.
168 Several empirical equations are available and have been presented in well-known reference
169 books in the industry [14] [15] Eq. (5).

$$\rho_{bath} \left[\frac{g}{cm^3} \right] = 2.64 - 0.0008(\text{temperature in } ^\circ C) + 0.18 \left(\frac{w\% NaF}{w\% AlF_3} \right) \quad (5)$$
$$- 0.008(w\% Al_2O_3) + 0.005(w\% CaF_2) + 0.008(w\% MgF_2)$$
$$- 0.004(w\% LiF)$$

170

171 The above-mentioned values represent well the parameters of the experimental setup used in
172 the present work and shall be used in the calculations.

173 The surface tension of cryolitic melts has been measured by several research groups by pin
174 detachment method [16] or maximum bubble pressure methods [12]. Model equations were
175 fitted to the experimental data Eq.(6). The validity of these empirical equations is limited to a
176 certain temperature range where the experiments were conducted. As the alumina fed into the
177 bath tends to be several hundred degrees cooler than the bath itself, surface tension values at
178 low temperature hold particular interest in the flotation of alumina rafts. Beside measurements,

179 a theoretical approach to predict the surface tension of molten salt mixtures is also available
180 [17].

$$\begin{aligned} \gamma_{bath} \left[\frac{mN}{m} \right] = & 266.69 - 0.1257t - 4.754(w\%AlF_3) + 1.546 \cdot 10^{-3} w\%AlF_3 \cdot t \\ & + 3.002 \cdot 10^{-2} \cdot w\%AlF_3^2 + 2.078 \cdot 10^{-5} \cdot w\%AlF_3 \cdot w\%CaF_2 \cdot t \\ & + 2.702 \cdot 10^{-5} \cdot w\%AlF_3 \cdot w\%Al_2O_3 \cdot t - 3.507 \cdot 10^{-4} \cdot w\%CaF_2 \\ & \cdot w\%Al_2O_3 \cdot t \end{aligned} \quad (6)$$

181

182

183 where t is the temperature in Celsius.

184 The equation (Eq. 6) predicts the surface tension to be 145 mN/m, at the chemical composition
185 and the temperature of the bath, during our experiments [16]. For the bath-metal interfacial
186 tension, 450 mN/m was used in the calculations [18].

187 For future reference, the capillary length (a), a scaling factor necessary to calculate surface
188 curvature, and interpreting dimensionless forms of the flotation model, is 2.6 mm at the upper
189 bath surface Eq. (7).

$$a = \sqrt{\frac{\gamma}{\Delta\rho g}} \quad (7)$$

190

191 The contact angle between alumina and aluminum on the BMI was measured by Utigard [20]
192 and was found to be between 150-170°. As the electrolytic bath dissolves alumina, it is expected
193 that alumina is wetted by the bath. However, the actual contact angle between these
194 substances has not been found in the literature.

195 **Experimental**

196 Setup

197 The high temperature experiments were conducted at the laboratory of the authors' research
198 group, GRIPS, UQAC, in a carbon crucible. The free surface of the bath was 7.6 cm x 7.6 cm
199 square with rounded corners. The depth of the bath was 3.8 cm. The prepared bath contained
200 83% cryolite, 11.5% AlF₃ and 5.5% CaF₂. Due to impurities, the initial alumina content was 3%.
201 The rectangular carbon crucible was placed in the heated chamber of an electric kiln, and
202 heated from three sides. The thermocouple for the temperature control was placed under the
203 crucible. The insulated cover from the top was removed during experiments, and replaced
204 between tests so the temperature could stabilize. For longer experiments, to reduce the heat
205 loss, the opening was covered with a quartz plate between manipulations to be able to observe
206 the test object on the bath surface. The control temperature usually was set to 980 °C, which

207 decreased after the removal of the cover. Periodically a thermocouple was inserted in the bath
208 and it showed that the temperature stabilized 10°C below the control temperature.

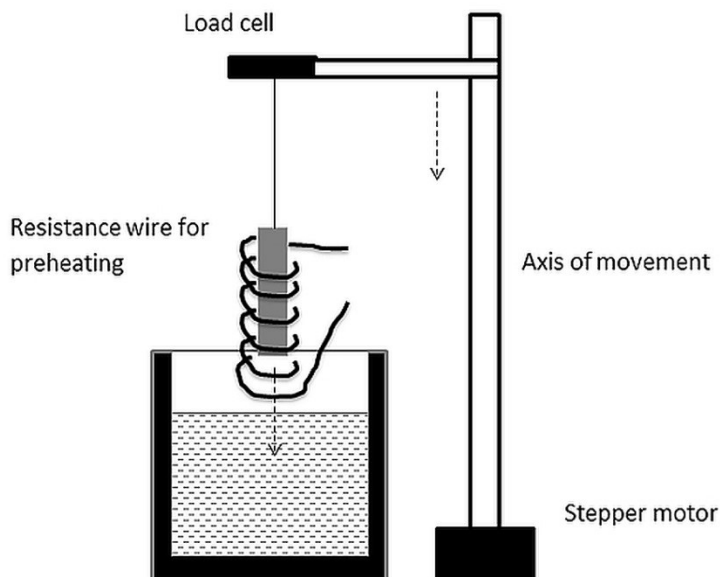
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210 Contact angle measurement

211 The contact angle is a necessary parameter to determine the conditions of flotation. As the
212 alumina-cryolitic bath contact angle has not been found in literature, it was necessary to obtain
213 it through experiments. The high temperature and corrosive nature of the bath renders visual
214 methods to determine contact angle nearly impossible. Another difficulty may rise from the low
215 superheat: bath would solidify in contact with insufficiently preheated alumina. Extended
216 contact between unsaturated bath and alumina leads to dissolution, changing the shape and
217 size of the alumina object.

218 The first attempts to measure the contact angle by the capillary rise method provided
219 inaccurate results. To improve precision, other tests with Wilhelmy method were prepared,
220 using the gravimetric system developed by GRIPS at UQAC [19].

221 The gravimetric system was developed to analyze different aspects of the behavior of alumina in
222 the cryolitic bath (Figure 3). Different test objects were suspended above the cryolitic bath. The
223 samples were descended at a predetermined velocity into the bath while their apparent mass
224 was measured by a load cell. Both the position and the apparent mass were recorded
225 simultaneously.



226

227

Figure 3: Schema of gravimetric system

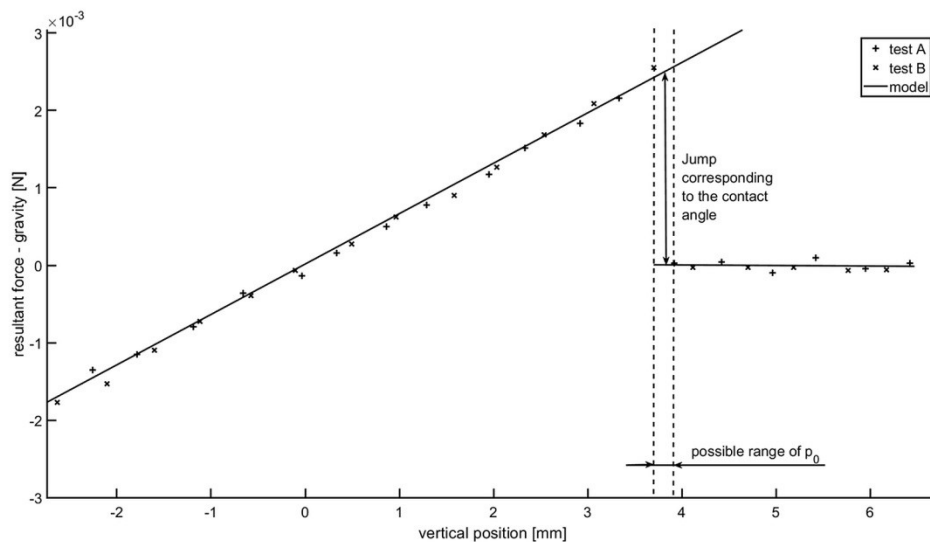
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229 An alumina rod of ¼ inch diameter was suspended by nichrome wire above the bath surface,
230 preheated to avoid bath solidification upon insertion, then descended with a velocity of 0.5
231 mm/s, the position and resultant force logged at 1 second intervals.

232 Before the test object touched the liquid surface (position larger than p_0), the force corresponds
233 to its mass. When the object reaches the surface, the resultant force increases rapidly (ΔF), due
234 to the effect of the surface tension. With further descent in the liquid (position below p_0) the
235 resultant force is decreased by the buoyant force.

$$F = m \cdot g + \begin{cases} 0 & \text{if } p = \text{position} > p_0 \\ d\pi\gamma \cdot \cos \alpha + \frac{d^2\pi}{4} \rho_l (p - p_0)g & \text{if } p \leq p_0 \end{cases} \quad (8)$$

$$\cos \alpha = \frac{\Delta F|_{p_0}}{d \cdot \pi \cdot \gamma}$$



236

237

238 Figure 4: Buoyant and surface tension forces acting on an alumina rod,
239 immersed into cryolitic bath

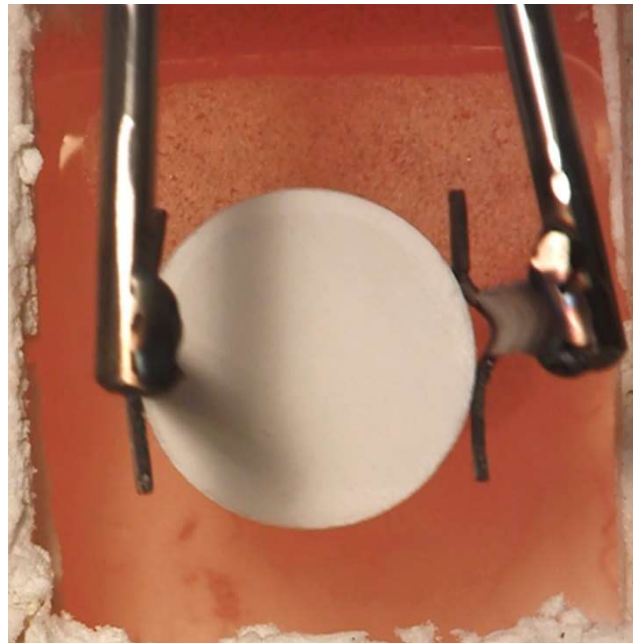
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241 Theoretically, the contact angle can be calculated from the jump in the resultant force when the
242 rod first touches the surface (p_0 , position 0). However, as the data is not continuous, the
243 detection of the jump may be delayed by almost a full-time step. To decrease this uncertainty,
244 the results of two tests (A and B) were overlapped (Figure 4). Note that as we cannot produce
245 perfectly identical samples, both the resultant force and the zero position need to be adjusted.
246 Vertically, one set of results was shifted with the force corresponding with the difference
247 between the initial masses of the samples, while the horizontal shifting aligned the left side of

248 the diagram. This process did not only provide better visual representation, but the exact
249 position of zero was narrowed down significantly. There is a slight noise in the data, but the test
250 results correspond well to the model, and it narrows down the range of the contact angle to a
251 range of 29-34°.

252 Compressed alumina discs as artificial rafts

253 Primary alumina discs (with 40mm diameter and 8.6 mm thickness) were prepared using a
254 Struers Labo-Press 3 machine. 12.5 ml powder was fed into the machine chamber, and exposed
255 to 50 kN for 15 minutes which included a 3 minutes initial period where the powder was heated
256 to 180 °C. The produced discs were very fragile, they crumbled easily and some powder got lost
257 every time during handling them. For this reason, a separate batch of discs was prepared only
258 for the statistical analysis of the properties of the discs. The average mass of a dozen discs was
259 13.4 ±0.2 g. The average mass loss after four manipulations (for example: taking it up and
260 putting it on a scale would count as one manipulation) was 1.2%. The average thickness of the
261 discs is 8.6 ±0.1 mm. The density derived from these measurements was 1.25 g/cm³ – while the
262 measured (tapped) bulk density of alumina powder used for the preparation of discs was 1.03
263 g/cm³, calculated by measuring the mass of a given volume of powder. Three successful series of
264 tests, noted `A`, `B` and `C` were each conducted consecutively with fresh cryolitic bath.



265

266

267 Figure 5: Insertion of alumina disc onto the bath surface

268

269 The compressed discs were placed on the surface of cryolitic bath (Figure 5), and after a certain
270 period of time, they were recovered. The apparent density of the samples was estimated by
271 measuring the thickness and diameter of the recovered discs, assuming perfectly cylindrical

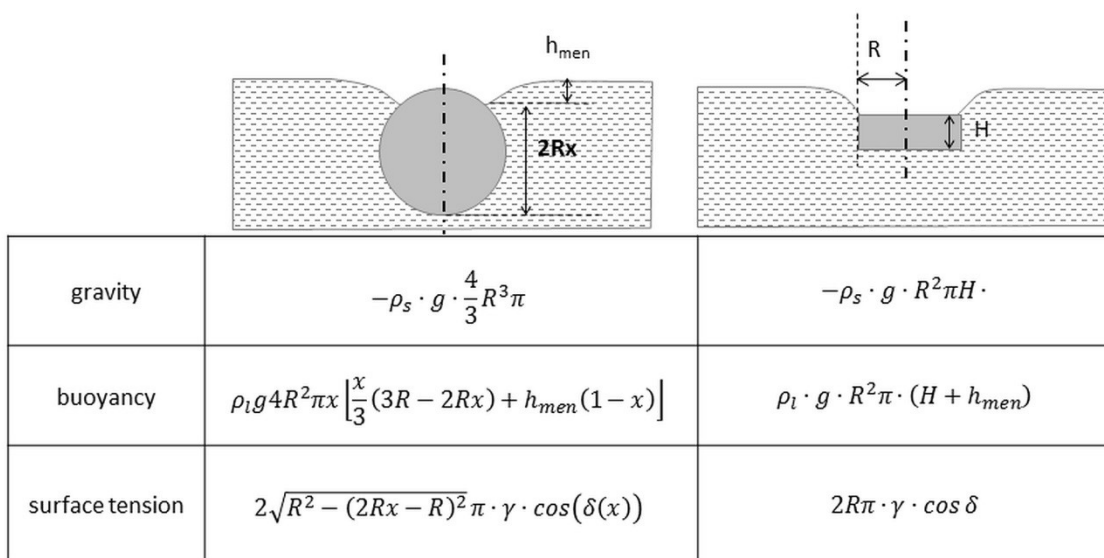
272 form, while in some cases, samples were covered with a silicon-based spray to obtain density
 273 with Archimedes method; by weighing of the impermeable sample suspended in water and in
 274 air.

275 Experiments on the bath-metal interface were attempted, but visual observation failed due to a
 276 rapidly developing aluminum fog in the cryolite following the addition of the metal. The
 277 formerly transparent cryolitic bath turned opaque, and the samples were hid from view under
 278 the bath surface. While the gravimetric method may be applied in the future to examine the
 279 flotation on the BMI, it is recommended to apply measures that help flatten the bath-metal
 280 interface.

281 **Mathematical model**

282 The mathematical model was developed for two shapes: spheres and circular disks. The former
 283 is used as a universal shape; it can represent a single alumina particle, or an agglomerate on the
 284 bath-metal interface. The disk form holds more interest with small height-diameter ratio, as
 285 alumina tends to spread on the bath surface, therefore a disc is a reasonably good
 286 representation of an alumina raft. Theoretically, the same equation can be applied for large
 287 height-diameter ratio, such as a rod, floating vertically. This, admittedly, is an unlikely, mostly
 288 unstable scenario to occur naturally, and since it has no relevance for the studied phenomena
 289 either, the height-diameter ratio in this study was limited to 1 and under.

290 The governing equations of flotation are presented below, along with the corresponding shapes
 291 (Figure 6).



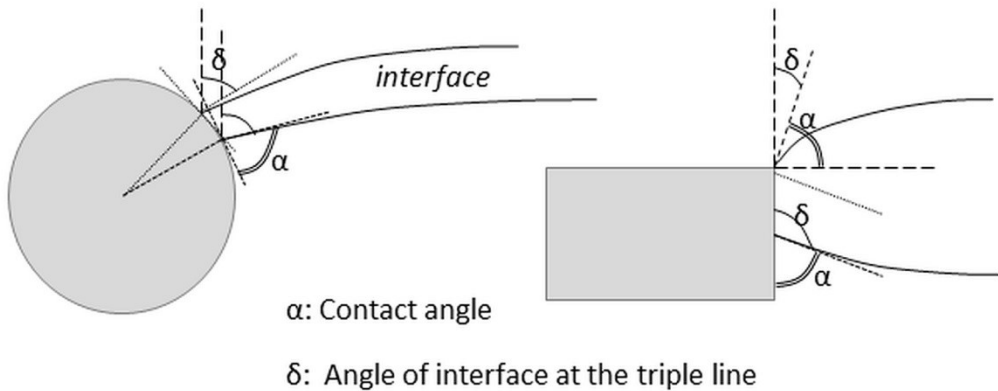
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294 Figure 6: Geometries and corresponding force terms used in the present flotation model

295 Where ρ_s is the density of solid,
 296 ρ_l is the density of liquid,
 297 R is the radius of the sphere or the disc, respectively
 298 H is the thickness of the disc
 299 x is the relative immersion of the sphere: the vertical distance between the triple line and the
 300 bottom of the sphere, in relation to its diameter
 301 and h_{men} is the meniscus height.

302 The characterization of the flotation limit as the maximum density with which an object can stay
 303 afloat on an interface, is more straightforward for disc geometry, as the length of the triple line
 304 is constant, and the position of the triple line at the flotation limit is evident. However, in the
 305 case of a sphere, the length of the triple line changes with the relative immersion (x), and so
 306 does the angle of the interface (Figure 7).



307
 308

309 Figure 7: Dependence of the angle of interface on the relative immersion with different
 310 geometries
 311 Based on the relative immersion of a sphere, x and the apparent contact angle α , the angle of
 312 the interface at the triple line can be expressed by the following equation.

$$\delta(x) = 2\pi - \arccos(1 - 2x) - \frac{\pi}{2} - \alpha \quad (9)$$

313

314 With disc geometry, the flotation limit shall be reached at total immersion, where the angle of
 315 the interface has a degree of freedom described by the earlier mentioned Gibbs extension to
 316 the Young-Dupre law (Figure 2). The meniscus height was determined by the numerical solution

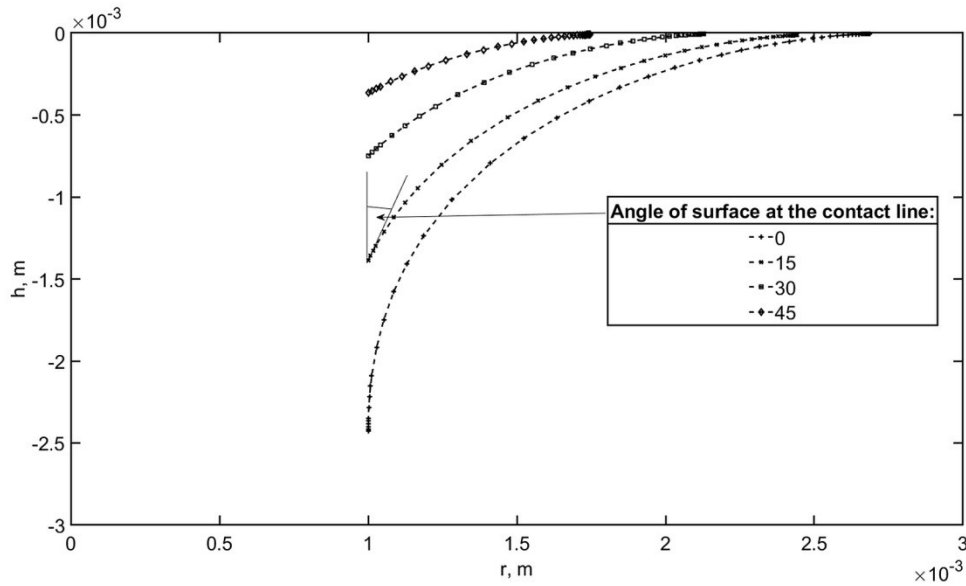
317 of the formerly presented equation (2). The following boundary conditions should apply,
 318 assuming a single floating object on an otherwise undisturbed surface:

$$\lim_{h \rightarrow 0} r(h) = \infty \tag{10}$$

$$\left. \frac{dr}{dh} \right|_{h=-h_{men}} = \tan \delta$$

319

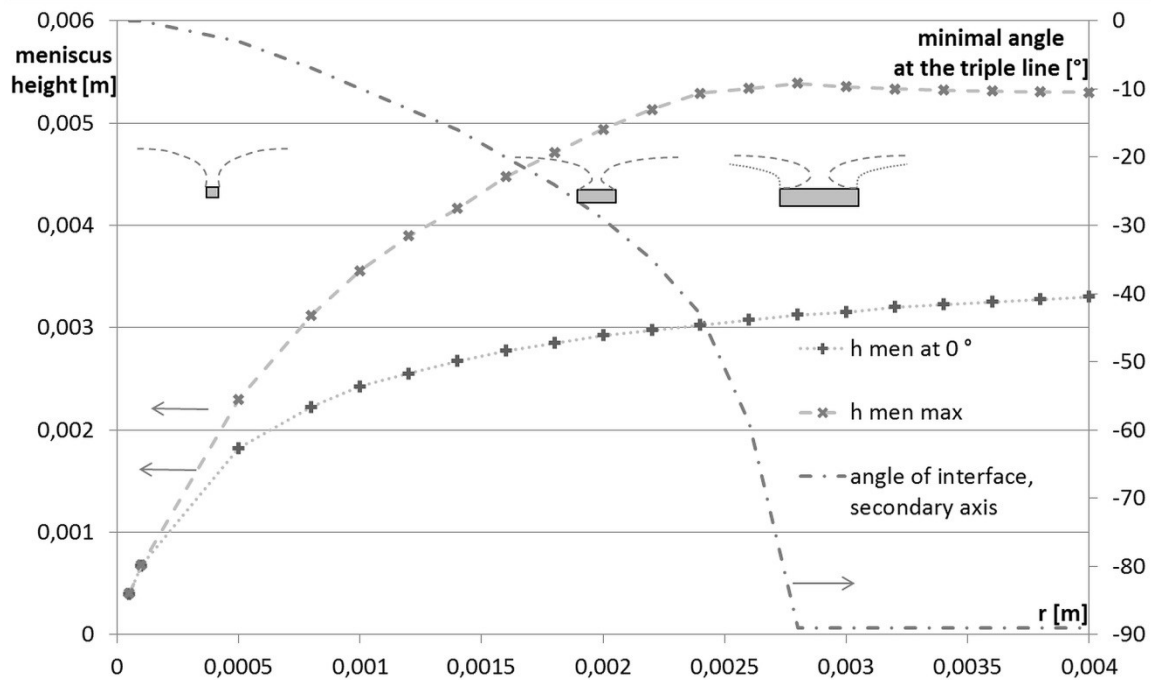
320 Due to the limitations of Matlab, and the fact that h_{men} was the sought parameter, a trial and
 321 error method was applied, and the meniscus height gradually decreased until the solution
 322 fulfilled (or rather, approached) the first boundary condition. Solutions for a few different
 323 variables are presented below (Figure 8).



324

325

326 Figure 8: Numerical solution of differential equation, shape of meniscus
 327 Regardless of the geometry of the object, the angle of the interface could potentially become
 328 negative, so as the interface would bulge over the floating object. This does not hinder the
 329 solution of the differential equation Eq. (2) (i.e. finding the shape of the interface) for larger
 330 diameters, but as the radius of the triple line fell below the capillary length, the range of angles
 331 for which acceptable solutions were found, became limited (Figure 9).



332

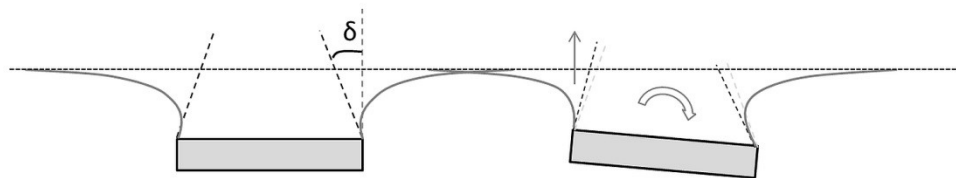
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Figure 9: Dependence of meniscus height on radius and angle of surface

334

It should be noted however, that researchers who attempted solving the problem of meniscus shape, did not succeed achieving negative interface angles with floating discs in reality, supposedly due to instability [2]. It stands to reason, that a position with negative surface angle would be unstable, and a slight tilt of the floating disc could swing the disc out of balance. As one side of the disc gets closer to the surface, the angle of surface of the contact line at that side gets closer to vertical, escalating the tilt. For this reason, the minimal angle of the surface for discs in the model was limited to 0 degree (Figure 10).

340



341

342

Figure 10: Unstable position of a floating disc

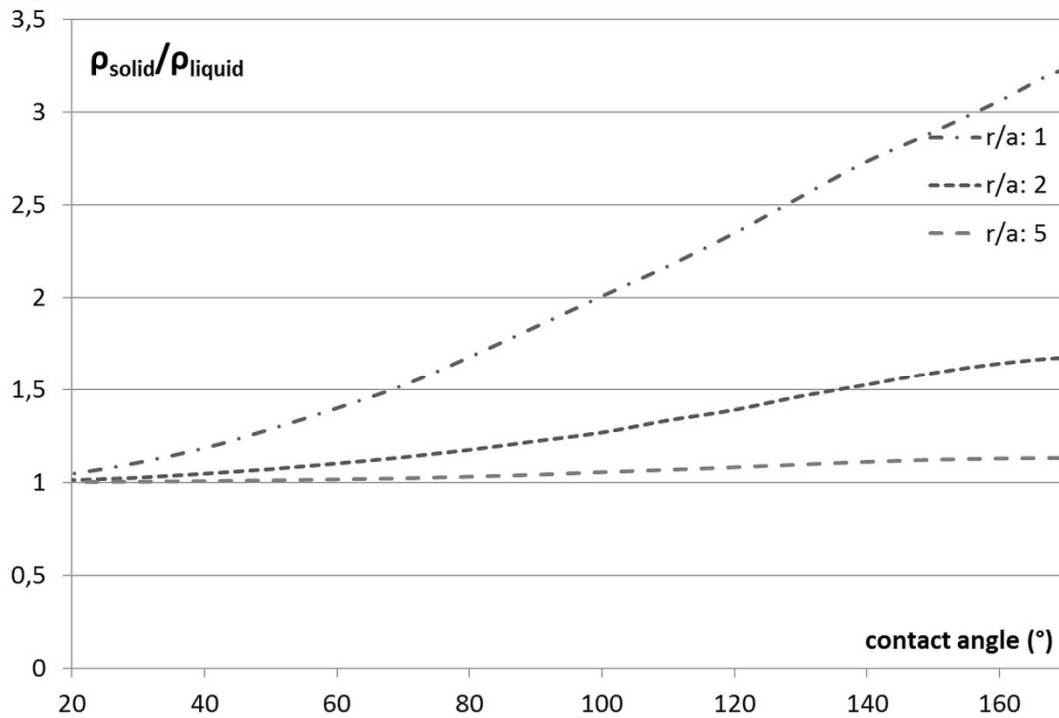
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While there is no possibility of stable floating position when the density of the solid exceeds the density of the liquid, metastable states exist, where depending on the magnitude of the disturbance, the degree of tilting or displacement from the equilibrium position, the floating object might return to its original floating position, or sink.

346

347 **Interpretation of results**

348 Firstly, the model results for flotation limit are presented in a general, dimensionless form
349 (Figure 11). The contact angle has an immense effect on the flotation limit of spheres. While in
350 case of perfect wetting, the density of a floating sphere could not exceed the density of the
351 liquid, the maximal density gradually increases with increasing contact angle, with a more rapid
352 rate in case of smaller dimensions (when the radius of the spherical object is at the same scale
353 as the capillary length).



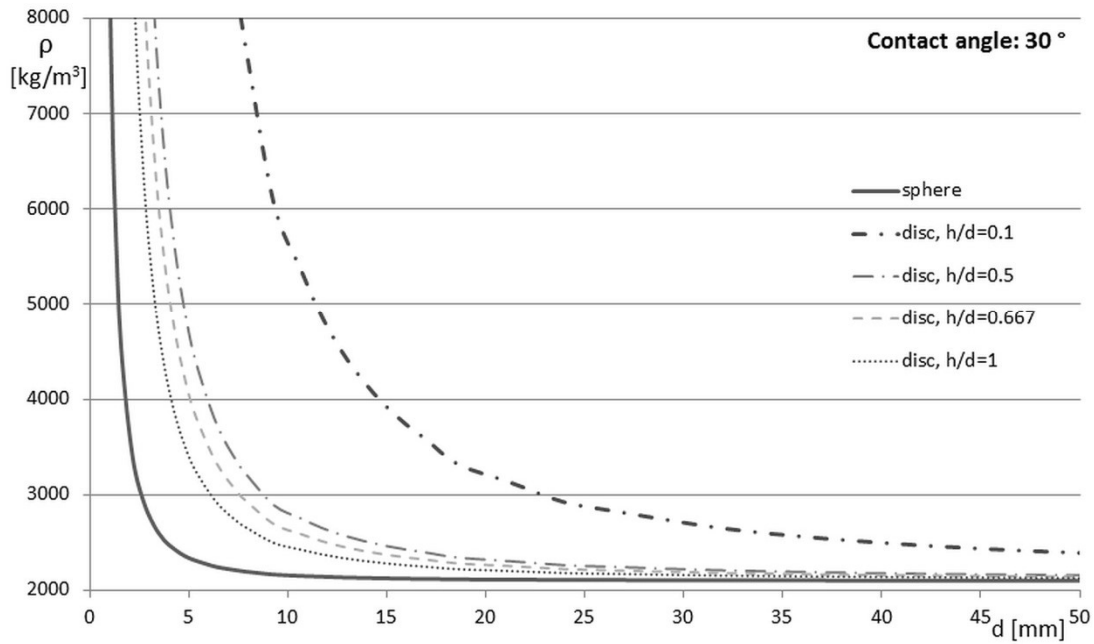
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Figure 11: Flotation limit of spheres

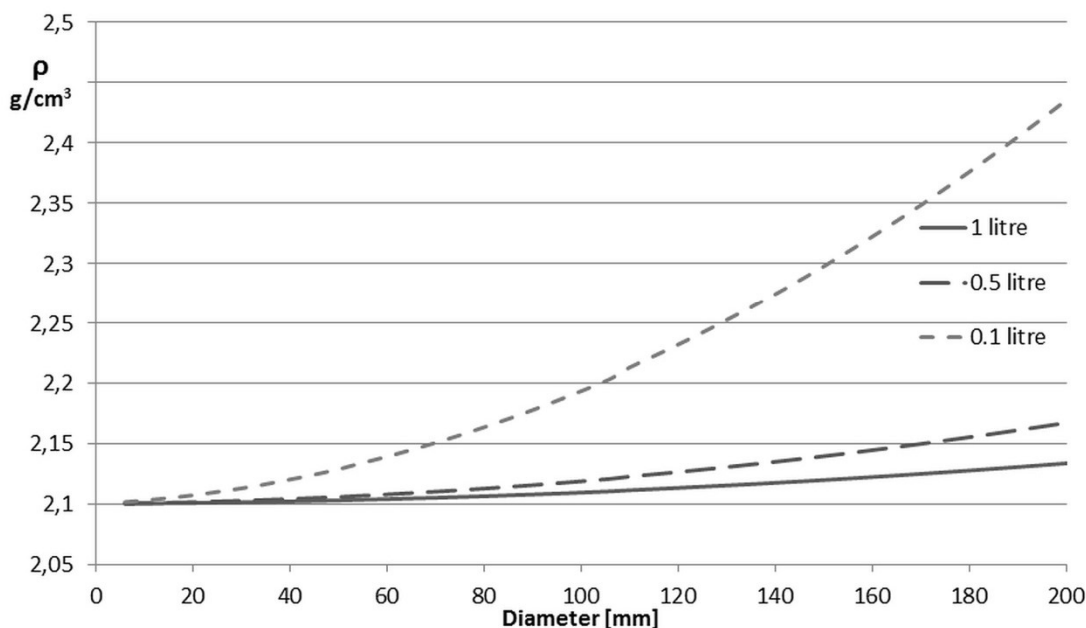
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357 For studying the behavior of solid disks and spheres on the upper surface of the bath, the
358 flotation limit was calculated for 30° contact angle. The effect of the small contact angle is more
359 prominent for the flotation limit of spheres than for discs. Discs would always have a higher
360 flotation limit than spheres with the same volume and diameter; and as the height-diameter
361 ratio decreases, the discs get thinner, the curved surface's contribution to the buoyant force
362 becomes more prominent, as can be seen in the increase of flotation limit with decreasing h/d
363 ratio (Figure 12).



364

365 Figure 12: Flotation limit on bath surface, contact angle: 30°
 366 Alumina powder tends to spread on the bath surface due to its moisture content that
 367 evaporates when it gets in contact with the molten electrolyte. Therefore, discs with small
 368 thickness-diameter ratios hold the most interest. The bulk density of alumina powder is around
 369 1 g/cm³, while the skeletal density of alpha alumina is almost 4 g/cm³. While cylindrical
 370 agglomerates with large height-diameter ratio could be expected to float if they are only a few
 371 mm in diameter, thin rafts could theoretically stay afloat easily.



372

373

374 Figure 13: Density limit of a fixed volume of alumina raft, assuming spreading to disc-shape
 375 In industrial electrolysis cells a certain quantity of alumina powder is injected to the bath surface
 376 at a time, usually between 0.5 and 2 kg, which corresponds to 0.5-2 l of volume. This powder
 377 tends to spread on the available surface, limited by the anodes. With these considerations, the
 378 density limit of flotation was calculated for disc-shaped alumina rafts (Figure 13). While the
 379 density of larger rafts could only slightly exceed the density of the bath before sinking, with
 380 smaller batch-sizes, the maximal density increases rapidly with the available surface for
 381 spreading.

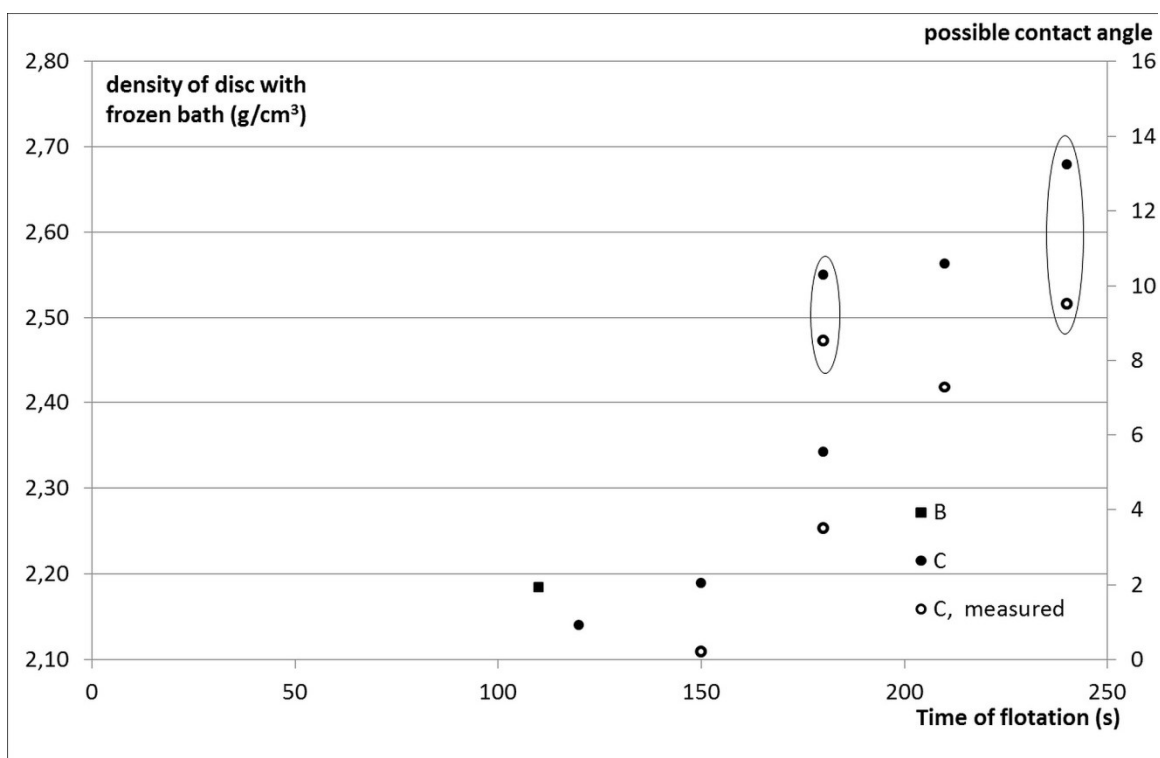
382

383 Comparison of model and experiments

384 The experiments proved that alumina discs can float on the surface of the cryolitic bath, even
 385 when their density became larger than the density of the bath, therefore the surface tension
 386 can play a role in the delayed dispersion of alumina in the bath. In the evaluation of the
 387 experiments, the mathematical model of flotation is used reversibly. When modeling the
 388 flotation, the maximal density of a floating object was calculated, based on its size and the
 389 contact angle. For the experiments, the density and dimensions of the floating discs are known,
 390 which, with the help of the mathematical model, provides the angle of the surface at the
 391 contact line, at the moment the disc was removed from the bath – and that points to the
 392 minimal contact angle (Figure 14). The discrepancy between the estimated and measured
 393 density are due to the fact that the discs were covered with an uneven layer of frozen bath,

394 partly due to the removal process. As the estimated volume was based on the diameter and
 395 thickness of the discs at their bottom corners, the volume was underestimated. While for the
 396 measurement of the volume with Archimedes method, the total volume was measured,
 397 including the added frozen bath, which adds to the volume, and, at that point of infiltration,
 398 decreases the overall density.

399 While the contact angle between alumina and bath was measured to be around 30° using the
 400 Wilhelmy method with an alumina rod, with the discs, only 10° was reached at best. This could
 401 be explained by several factors relating to the realities of experimentation, such as the lack of a
 402 well-defined, sharp edge of the discs, slight asymmetries in either the alumina discs or the
 403 setup, and the continued exposure to disturbances, the convection in the bath, and
 404 manipulations around the setup.

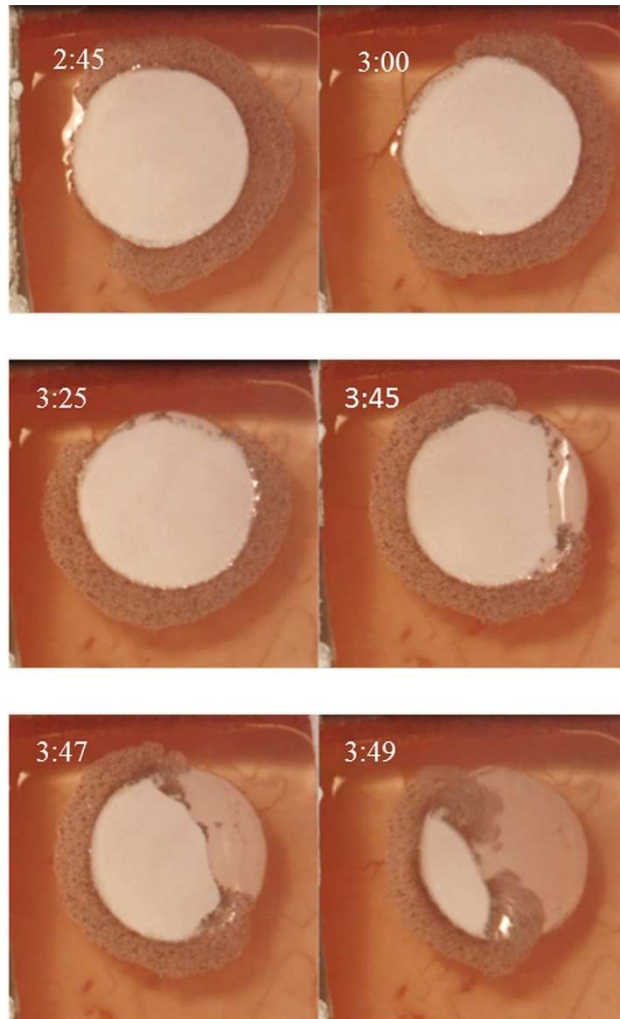


405

406 Figure 14: Density of samples, results from repeated experiments B and C

407 The video recordings of the experiments also show an influential factor, unaccounted for in the
 408 mathematical model: the presence of carbon and other particles on the bath surface, originating
 409 from the degradation of the carbon crucible and from the refractory walls. As the selected series
 410 of images show (Figure 15), the surface starts creeping over the disc at the side that is clear of
 411 scum. While the impurities on the left side hold the liquid surface at bay, the latter creeps upon
 412 the disc on the right with an accelerating rate, causing its eventual submersion.

413



414

415

416 Figure 15: Compressed alumina disc, process of sinking; time after insertion marked (mm:ss)

417

418 **Conclusions**

419 The contact angle between alumina and cryolitic bath was measured, and a range of 29-34° was
 420 determined.

421 A mathematical model was developed to investigate the conditions of static flotation of
 422 axisymmetric objects on a liquid surface. Two geometry, disc and sphere, were considered. The
 423 model was specifically applied to the parameters encountered in an aluminum electrolysis cell,
 424 to analyze the flotation limit of alumina rafts, forming on the bath surface upon the injection of
 425 alumina powder. The flotation limit was defined as the maximum density for a floating object of
 426 a given size; alternatively, the flotation limit could be formulated as the maximum size of a
 427 floating solid for a given density. It was shown how the expected shape, size and density of

428 alumina rafts and agglomerates could influence their flotation. Realistic sizes of alumina batches
429 were considered and the effect of spreading on the flotation was presented.

430 Besides a mathematical model, experiments with artificial alumina rafts were conducted on the
431 surface of cryolitic bath. While the theoretical flotation limit for compressed alumina discs has
432 not been reached in the experiments, it was only expected since perfect edges and symmetry is
433 unobtainable in reality, nevertheless, the contribution of the surface tension to the flotation was
434 shown.

435 The experiments brought attention to the influence of solid particles on the bath surface on
436 flotation which justifies further investigations. Also, an experimental study of the flotation on
437 the bath-metal interface has not been realized yet, future efforts will be needed to overcome
438 the experimental difficulties.

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442 **Bibliography**

443

444 [1] C. Kaszas, L. Kiss, S. Guerard and J.-F. Bilodeau: *TMS Light Metals*, 2015, pp. 639-644

445 [2] P. Singh and D. D. Joseph: *Fluid Mechanics*, 2005, vol. 530, pp. 31-80

446 [3] A. Solheim and S. Rolseth: *TMS Light Metals*, 2001, pp. 469-474

447 [4] Pushpendra Singh, Daniel D. Josep and Nadine Aubry: *Soft Matter*, 2010, no. 6, pp.
448 4310–4325

449 [5] Victor. M. Starov, Manuel G. Velarde, Clayton J. Radke: *Wetting and Spreading*
450 *Dynamics*, Surfactant Science Series vol 138, 1st ed., CRC Press, 2007.

451 [6] J. Thonstad and Y.-X. Liu: *TMS Light Metals*, 1981, pp. 303-312

452 [7] D. Bunyak: *Mining History Journal*, 2000, pp. 35-45

453 [8] B. Kowalczuk Przemyslaw and J. Drzymala: *Colloids and Surfaces A: Physicochem. Eng.*
454 *Aspects*, 2012, 393, pp. 81– 85.

455 [9] Daniel Chipfunhu, Massimiliano Zanin, Stephen Grano: *Minerals Engineering*, 2011, 24, pp.
456 50–57.

- 457 [10] P. B. Kowalczyk, O. Sahbaz and J. Drzymala: *Minerals Engineering*, 2011, 24, pp. 766–
458 771.
- 459 [11] David I. Walker: Alumina in aluminium smelting and its behaviour after addition to
460 cryolite-based electrolytes, PhD thesis, 1993, University of Toronto
- 461 [12] M. Kucharik and R. Vasiljev: *Z. Naturforsch*, 2006, no. 61a, pp. 389 – 398
- 462 [13] A. Solheim: *TMS Light Metals*, 2002, pp. 225-230
- 463 [14] J. Thonsta, Pavel Fellner, Geir Martin Haarberg, Jan Hives, Halvor Kvande, Asmund
464 Sterten: *Aluminium Electrolysis - Fundamentals of the Hall-Heroult Process*, 3rd ed., Aluminium-
465 Verlag, Dusseldorf, 2001, pp. 87-114
- 466 [15] K. Grjotheim and H. Kvande, *Introduction to Aluminium Electrolysis*, 2nd ed., Aluminium-
467 Verlag, Dusseldorf, 1993, pp. 60-85
- 468 [16] V. Danek, O. Patarak and T. Ostvold: *Canadian Metallurgical Quarterly*, 1995, vol. 34, no.
469 2, pp. 129-133
- 470 [17] M. Vermot Des Roches, Modèles de tension de surface pour les sels fondus et les
471 métaux liquides appliqués au procédé Hall-Héroult, master thesis, 2018, University of Montreal
- 472 [18] T. Utigard and J. M. Toguri, *METALLURGICAL TRANSACTIONS B*, 1985, Vol 16B, p 333-338
- 473 [19] J. Alari, L. Kiss, S. Poncsak, T. Roger: The Encyclopaedia of Research on Aluminium in
474 Quebec 2018, REGAL Students' Day Aluminium Research Centre – REGAL, pp15
- 475