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BEHAVIOR OF POWDERS ON THE SURFACE OF A LIQUID

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Abstract

Agglomerates in the Hall-Héroult cell reduce the alumina dissolution rate and affect the stability of the process. Alumina agglomerates have been thoroughly studied, however their formation is not completely understood yet. This study focuses on the behavior of powders on the surface of a liquid, in an attempt to shed light on how alumina powder enters the electrolytic bath, as it could influence the formation of agglomerates.

The ability of an object to float on the surface of a liquid could be determined by analyzing the force balance. Besides liquid properties, the shape of the object, bulk density and contact angle were analyzed. Beyond the analysis of single particles, the condition of floating of particle agglomerates was also examined, which could lead to the deeper understanding of the behavior of powders on a liquid surface and to a more accurate modeling of alumina feeding into the bath.

Introduction

Researches on alumina dissolution usually focus on the properties of alumina [1, 2, 3] and the properties of the electrolytic bath [4]. Although we are aware that alumina powder could float on the molten bath, the phenomenon and its effects were not thoroughly investigated yet. While relevant articles note that alpha-alumina sinks and gamma-alumina floats [5], or provide tables about the duration of floating of several different types of alumina powders [6], they do not elaborate on the why and how of the matter. Researches related to both surface tension and Hall-Héroult cells are directed towards the aluminum-bath interface. [7, 8]

Flotation is used in the mineral industry to separate ores. The treatment may involve hydrophobic additives and aeration, so the particles would get attached to bubbles, rise to the surface and stay there. Experiments are usually aimed to get a recovery rate of a powder and their approach is more practical than theoretical. [9, 10, 11]

In this paper an attempt is made to improve the understanding of the powder flotation and specially the alumina feeding from a different point of view.

Force balance of a single floating particle

A single particle on the surface of a liquid is in equilibrium only if the forces applied to it cancel each other out. This may even occur when the density of the particle is higher than the density of the liquid - due to surface tension. (Figure 1.)

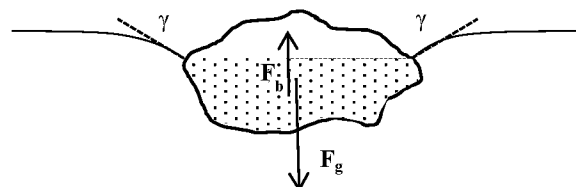


Figure 1. Floating particle on the surface of a liquid

Three forces should be considered when calculating the force balance of a particle: gravitational force,

$$F_g = V_p * \rho_p * g \quad (1)$$

buoyancy force,

$$F_b = V_i * \rho_l * g \quad (2)$$

and the resultant force of the surface tension,

$$F_s = l * \gamma * \cos(\delta) \quad (3)$$

where V_p is the volume of the particle, ρ_p is the density of the particle, g is the gravitational constant, V_i is the immersed volume of the particle, ρ_l is the density of the liquid, while γ is the surface tension, l is the length of the line of contact (triple line), and δ is the angle of surface along the triple line, measured relative to the vertical.

The angle of the surface tension is not the contact angle, but is closely related to it (see Figure 2). The surface tension force that acts along the triple line depends on two factors: the slope of the particle contour at the contact line and the contact angle. It is worth mentioning that the surface tension might act upwards or downwards depending on the shape of the particle and the contact angle. The horizontal components of the surface tension should cancel each other out or else the particle would not be in equilibrium.

The immersed volume to calculate buoyancy shall be considered in this paper as the volume of the particle below the contact line. Other researchers either have neglected buoyancy [8], or applied it to the volume below the undisturbed surface of the liquid [12], which results in a greater buoyant force in case of a flotation aided by surface tension. Others choose an another approach leading to a smaller buoyant force [7] than our calculations.

Force balance of a spherical particle

The chosen form for the floatability study was the sphere. As mentioned above, knowing the slope of the immersed particle at

the contact line is necessary to calculate the angle of the surface tension. (Figure 2.)

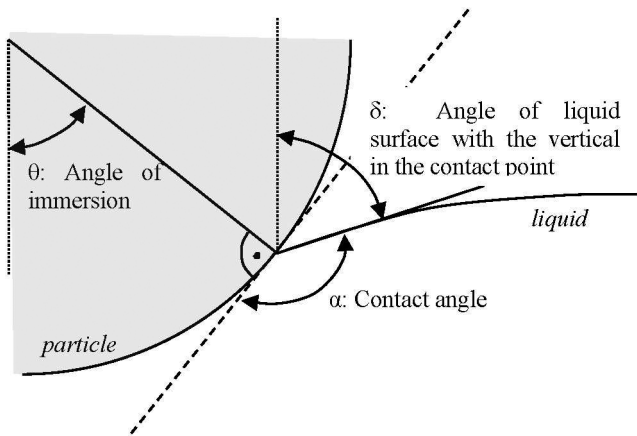


Figure 2. Determining the angle of the surface tension in case of a spherical particle

The force balance of a spherical particle immersed in a liquid can be written based on the former equations (1,2,3) and bearing in mind the geometry of the sphere.

$$\begin{aligned} & \gamma * 2\pi\sqrt{R^2 - (R - 2Rx)^2} * \cos(\delta(x)) \\ & + \rho_l \frac{\pi(2Rx)^2}{3} (3R - 2Rx)g \\ & - \rho_p \frac{4}{3}R^3\pi g = 0 \end{aligned} \quad (4)$$

Where x is the relative immersion compared to the diameter of the sphere. The angle of surface tension depends on the immersion of the particle as well (Figure 1.):

$$\delta(x) = 2\pi - \arccos(1 - 2x) - \frac{\pi}{2} - \alpha \quad (5)$$

Supposing we know the properties of the liquid and the particle, the relative immersion of the floating particle in equilibrium could be found if there is an x between 0 (particle practically not touching the surface) and 1 (complete immersion) that fulfills the equation.

The equation could be converted to the following form:

$$\frac{\gamma * 3/2\sqrt{4x - 4x^2} * \cos(\delta(x))}{\rho_p R^2 g} + \frac{\rho_l x^2 (3 - 2x)}{\rho_p} = 1 \quad (6)$$

This dimensionless form reveals which ratios of properties should be respected in case of an analogue model.

Floatability of a spherical particle

For a better illustration, instead of the forces, the potential energy of the particle was used to demonstrate the floatability. The potential energy was determined with a definite integral from x=0 to x – as the particle is slowly descending in the liquid.

$$E_p(x) = \int_{x=0}^x \sum F(x) dx \quad (7)$$

Plotting the potential energy in the function of immersion and the equilibrium position(s) of the given spherical particle appears where the slope of the curve is zero. In case of a local maximum, the equilibrium is unstable, while a local minimum signifies a stable or metastable position. When the density of the particle is higher than the liquid, the particle will eventually sink, if a disturbance is large enough. Less dense particles will keep rising back to the surface to regain their original position. If the curve does not flatter, then the particle will definitely sink. (Figure 3.)

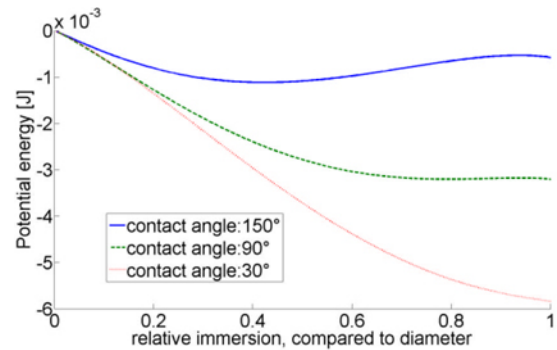


Figure 3. Spherical particle on the surface of a liquid, diameter 5 mm, surface tension:145 mJ/m², density of particle:3.55g/cm³, density of liquid: 2.1 g/cm³

Of the parameters influencing the floatability of the particle, the contact angle is the most peculiar. While the other parameters are materials properties, contact angle depends on all materials involved. Data are scarce and accuracy of measurements is debatable as it would require a perfectly smooth surface. It is all the more unfortunate as contact angle influence greatly the equilibrium position and the overall floatability of the particle. (Figure 4.)

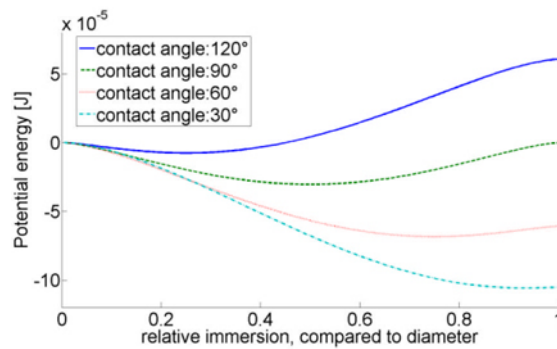


Figure 4. Spherical particle on the surface of a liquid, diameter 200 μm, surface tension 145 mJ/m², density of particle 3,55 g/cm³, density of liquid 2,1 g/cm³

Contact angle basically determines the equilibrium position of a small spherical particle. The immersion increases faster as the particle size reaches the limit of floatability – sinking is indicated by the vertical lines. (Figure 5.)

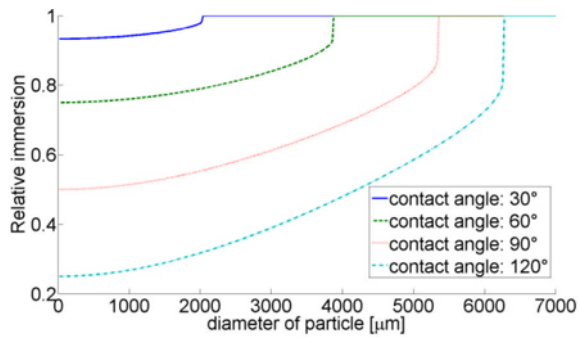


Figure 5. Immersion of a spherical particle on the surface of a liquid, surface tension 145 mJ/m², density of particle 3,55 g/cm³, density of liquid 2,1 g/cm³

Limit of floatability of a spherical particle

The question essentially would be: what is the largest particle that could float on the surface of a liquid? The largest size was determined by increasing the diameter as long as there was a position where the first derivative of E_p was still 0. The results in the function of contact angle are shown below. (Figure 6.) Even if these particles have the ability to float they would likely sink for the slightest interference.

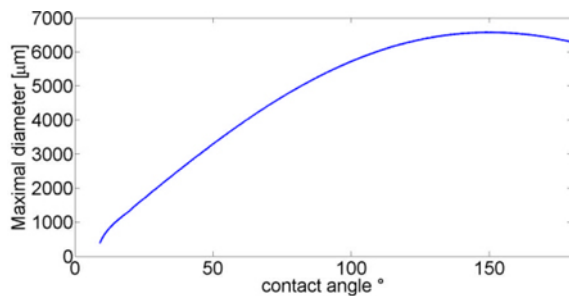


Figure 6. Size limit of spherical particle on the surface of a liquid, surface tension 145 mJ/m², density of particle 3,55 g/cm³, density of liquid 2,1 g/cm³

A simplified equation to determine the critical radius of a floating sphere was derived by Maru [8]:

$$R_{crit} = \frac{1,27}{\sqrt{\frac{g \cdot \Delta \rho_l - g \left(\frac{\Delta \rho_p - g}{\Delta \rho_l - p} - 1 \right)}}} \quad (8)$$

where $\Delta \rho$ symbolizes the density difference between the phases. The result, for the same properties as in figure 5, is a diameter of 5,6 mm which roughly corresponds to our results which is less than 6,5 mm, depending on the contact angle.

Surface quality and contact angle

The model so far was respecting the Young-Dupré law, supposing a perfectly smooth surface, where the equilibrium contact angle is constant and theoretically could be calculated with the interfacial energy between the three connecting phases. The reality, however,

is never perfect. The imperfections of the surface result in the apparent violation of the law.

At sharp corners the angle of the liquid surface is not predetermined by the Young-Dupré law, but the range within it stays as specified by Gibbs (Figure 7.) [12]

$$\alpha_0 < \alpha < 180 - \beta + \alpha_0 \quad (9)$$

Where α_0 is the equilibrium contact angle and β is the angle of the corner of the solid body.

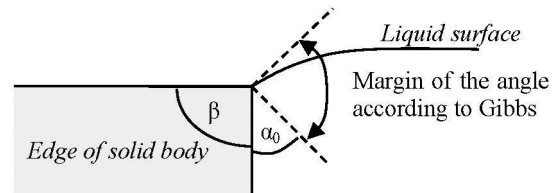


Figure 7. Illustration for Gibbs extension to Young-Dupré law

In practice, contact angle on a solid, relatively smooth surface can change between two extremities, the advancing and the receding contact angle. Advancing contact angle is obtained when the contact line is advancing toward the dry surface – it could be induced by adding liquid to a drop or lowering a plate in the liquid – while the opposite action will result in achieving the receding contact angle. The difference between these two values is called the contact angle hysteresis.

The best known and mostly accepted theories related to this phenomenon are the Wenzel and the Cassie-Baxter models. (Figure 8.)

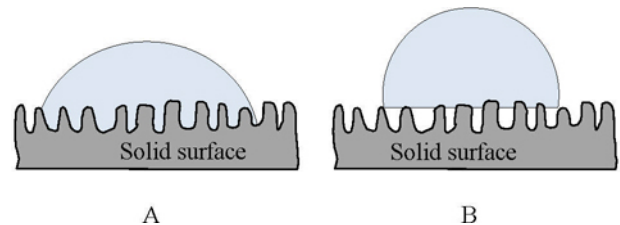


Figure 8. A. Wenzel B. Cassie-Baxter state of wetting

Wenzel proposed the modification of the Young equation, introducing a multiplier of the cosine of the contact angle to indicate the increased area caused by surface roughness. Cassie and Baxter developed their model to composite surfaces, and suggested that the cosine of the apparent contact angle would be the proportional sum of the cosine of the different material's contact angle. [13,14,15,16]

Alumina agglomerates

While all the other properties of alumina and molten electrolytic bath necessary for the calculations above, are already measured, contact angle between them has not been found in the literature. There are several methods for measuring the angle of contact between a liquid and a solid, but the extremely high temperature of the bath makes these measurements more difficult. The contact angle between alumina and the bath is probably significantly smaller than 90°, but the quality of the surface can have a great impact on the apparent surface angle.

There are other issues concerning the validity of the model as well. Although alumina could be approached as a smooth sphere [4], the exact shape of alumina particles are hard to describe. Comparing the specific surface area to the average particle size and it is obvious that alumina particles are not smooth, solid spheres. Pictures made with scanning electron microscope of various alumina powders are available from different sources. [17, 18, 6, 19] The general shape of an alumina particle is not fundamentally different from a sphere, but it is porous and laced with edges.

In the former calculations, particle density was set to the particle density of alumina, but air trapped inside the pores, evaporating water and freezing bath all decrease the density of the agglomerate. (Figure 9.)

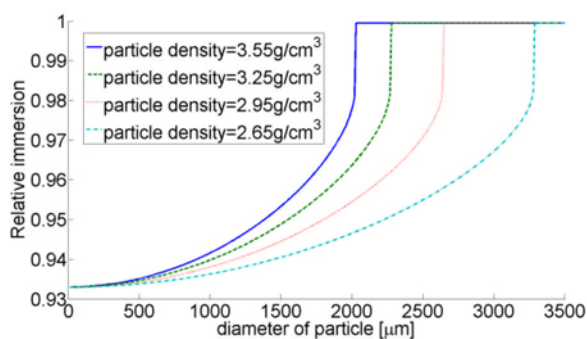


Figure 9. Immersion of spherical particle on the surface of a liquid, surface tension: 145 mJ/m², density of liquid: 2.1 g/cm³, contact angle: 30°

At small sizes, the particle density does not influence greatly the equilibrium position of the particle but it changes as the diameter is increasing, and there is significant difference in the size limit of flotation.

Discussion

The difficulty of an accurate flotation model of alumina lies in the uncertainty of contact angle and the irregular shape and unknown surface quality of the particles. In such a situation, instead of accuracy, functionality might be the priority.

The important characteristics of alumina powders for the model development shall be the angle of repose, as it depends greatly on the surface roughness, which influences the apparent contact angle as well. Beside the angle of repose, bulk density and BET surface area should be considered as they might indicate the amount of air captured in the powder during injection, decreasing the average density of the dose and prevent wetting.

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