

Flotation and Infiltration of Artificial Alumina Rafts on the Surface of Molten Cryolite

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Abstract

Alumina powder injection into the electrolytic bath usually involves raft formation: the alumina spreads on the surface of the electrolyte while the bath temporarily freezes around the powder. It stays afloat on the surface until the infiltration of the alumina by the bath and disturbances (agitation, splashing of liquid) lead to the sinking of the raft. Compressed discs of secondary alumina were prepared and inserted on the surface of molten cryolitic bath as artificial rafts for certain periods of time, to observe the flotation of the disc, the form and thickness of the frozen bath layer and the infiltration of alumina by the bath. Several sets of tests were conducted. The apparent densities of the discs were calculated to determine the role of surface tension in the flotation of the discs.

Keywords: Alumina raft; artificial alumina raft; flotation of alumina raft; infiltration of alumina raft; frozen bath.

1. Introduction

Although it is well known in the industry that alumina powder could float on the molten bath, the phenomenon and its effects have not been thoroughly investigated yet. Research in this field mostly aims to determine and model the dissolution rate of alumina and its dominant driving mechanisms. The investigated parameters influencing the dissolution are mostly the properties of alumina and the electrolytic bath [1 - 4]. Relevant articles noted that alpha-alumina sinks and gamma-alumina floats [5]. Townsend [6] provided tables about the duration of flotation of several different types of alumina powders, differentiated between soft (snow-like, low mechanical strength) and hard (ice-like, high mechanical strength) crust, but did not find clear correlation between crusting tendencies and other, easily measurable properties of the powder. Walker [7] reported in his dissertation that the consistency of an alumina raft, or a “floating island” as he put it, is mushy after 15 seconds in the bath. Its structure was found to be composed of three different layers, namely the solidified electrolyte, alumina infiltrated by the electrolyte with changing composition and dry alumina. Also, pockets of infiltrated alumina in frozen bath were found in the layers. He attributed the sinking of agglomerates (sub-islands) to the breaking of the island caused by mechanical interferences, like the splashing of the bath or another alumina injection.

Even if the structure of compressed alumina discs differs slightly from that of injected, more loose alumina raft, it was chosen to eliminate the haphazardness of rafts created by regular

feeding method, to ensure that the raft could be taken out entirely and the samples shall be comparable to each other – and also to compare its behavior to the results of a mathematical model of the raft.

2. Experimental Setup

Smelter grade alumina was compressed into discs, placed on the surface of cryolitic bath. Then, after a certain period of time, they were recovered with tongs specially made for this job. The samples obtained this way have been weighed and broken or cut up along the diameter for observing the infiltration front with an ‘Innovation beyond Imagination’ USB Digital Microscope and for further analysis with a Scanning Electron Microscope (SEM JEOL JSM 6480 LV with EDS Oxford SiLi detector and Inca software).

2.1. Alumina discs

Secondary alumina discs (with 40 mm diameter and 8.6 mm thickness) were prepared using a Struers Labo-Press 3 machine. 12.5 mL powder was fed into the machine chamber, and exposed to 50 kN for 15 minutes which included a 3 minutes initial period where the powder was heated to 180 °C. The resulting bulk density of alumina powder was not a precisely defined value. It depended on the actual arrangement of the particles, and therefore the mass and thickness of the discs had some dispersion. The discs were very fragile, they crumbled easily and some powder got lost every time they were handled. For this reason, a separate batch of discs was prepared only for the statistical analysis of the properties of the discs.

2.2. Bath properties

The cryolitic bath was melted in a carbon crucible; the free surface of the bath was 7.6 cm x 7.6 cm square with rounded corners. The depth of the bath was 3.8 cm. The prepared bath contained 83 % cryolite, 11.5 % AlF_3 and 5.5 % CaF_2 but due to the presence of some impurities in the bath and the experimental setup prior to the insertion of discs, as well as due to the partial dissolution of the discs themselves, the concentration of alumina was not constant. The estimated alumina concentration for each series of insertions will be indicated in the next section; any change due to bath evaporation was neglected.

Occasionally a thermocouple was inserted in the bath and it showed approximately 10°C less than the thermocouple inserted in the bottom of the crucible. After insertion the temperature was decreasing due to the cold disc, but at some point it is inevitable and the small size was cost-effective and convenient for manipulations. To reduce the heat loss towards the open surface of the bath, the opening was covered with a quartz plate between the insertion and recovery of the discs.

2.3. Series of experiments

The details of the different experiments are presented in Table 1.

Table 1. Parameters of experiments.

	Initial alumina concentration of bath %	Temperature of crucible °C	Flotation times of discs (s)
A	5,5	982	30, 60, 90
B	4,2	992	40, 90, 20, 70, 120, 60

(2 days)	4,2	992	110, 30, 80, 10, 50, 100
C	4,2	992	120, 210, 30, 150, 60, 240, 90, 180*

*Sunk, repeated in next experiment, same conditions, stayed afloat.

3. Results

3.1. Alumina discs

The average mass of a dozen discs was 13.4 g, with a deviation of +/- 0.2 g. The average mass loss after four manipulations (for example: taking it up and putting it on a scale) was 1.2 %. The average thickness of the discs is 8.6 mm, with a deviation of +/- 0.1 mm. The density derived from these measurements was 1.25 g/cm³ – while the measured bulk density of alumina powder used for the preparation of discs was 1.03 g/cm³, calculated by measuring the mass of a given volume of powder.

3.2. Course of insertion and recovery

Both the insertion and the recovery were executed with tongs specially designed for this task.

Right after the insertion, as the adsorbed and chemically bound water was evaporating. The vapor was leaving the alumina, bubbles were growing and in some cases vigorously moving around the discs in the bath, but none of the discs lost its integrity in the process.

The quartz plate covering the top of the crucible after the insertion became hazy rapidly due to the deposition of vapor emitted by the bath, so it was changed frequently to maintain the visibility of the floating discs.

Recovery was the most challenging part of the experiment. A careless movement could cause premature sinking of the disc, or it could slip and fall back into the bath. However these mishaps also led to observations. It was witnessed that right after sinking big gas bubbles left the disc as the upper, formerly non wetted but preheated powder particles got infiltrated rapidly by the bath. These bubbles in some cases also led to the removal or displacement of that upper part of the disc.

3.3. Structure of samples

The recovered alumina discs partially kept their original brittle, powdery structure in the upper-middle part, but the edge and the bottom were hardened due to the infiltration and possible sintering.

A frozen layer of bath could be observed on most of the samples, but with longer flotation times, the frozen layer re-melted, it got gradually thinner and more brittle, therefore even if it had existed, it disappeared sometimes. The black/grey impurities stuck on the samples were carbon grains floating on the bath surface, originated from the crucible.

The alumina which was not in direct contact with the bath disintegrated when the disc was cut or broken up for analysis, which left the infiltrated powder and the frozen layer to study (Figure 1).



Figure 1. Left: Photo of alumina disc after recovery from the bath, Right: Microscope photo of the cross section of the edge (series A, secondary alumina, 30 s)

3.4. Infiltration of alumina by the bath

The samples from series A were analyzed by scanning electron microscope (SEM). While with optical microscope the porosity of the infiltrated powder was not very apparent, on the SEM images it was clearly seen that the infiltration was not uniform. The corner was very dense and compact while porosity increased towards the zone formed by loose powder. It can also be seen on the upper part of the photo, which was the bottom of the disc, how the frozen layer started to erode due to polishing (Figure 2).

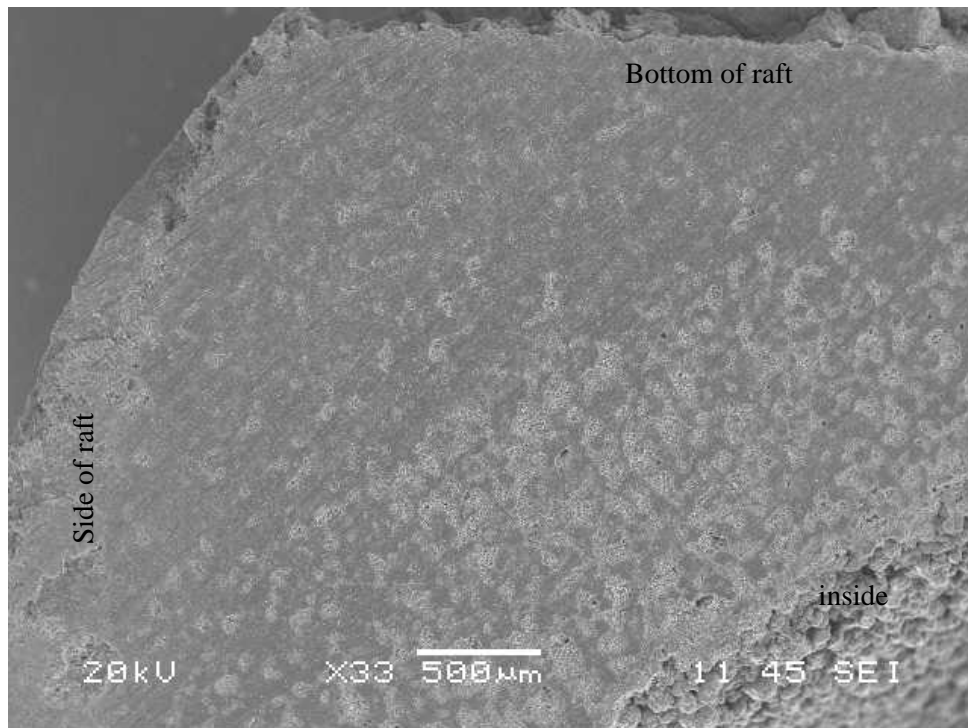
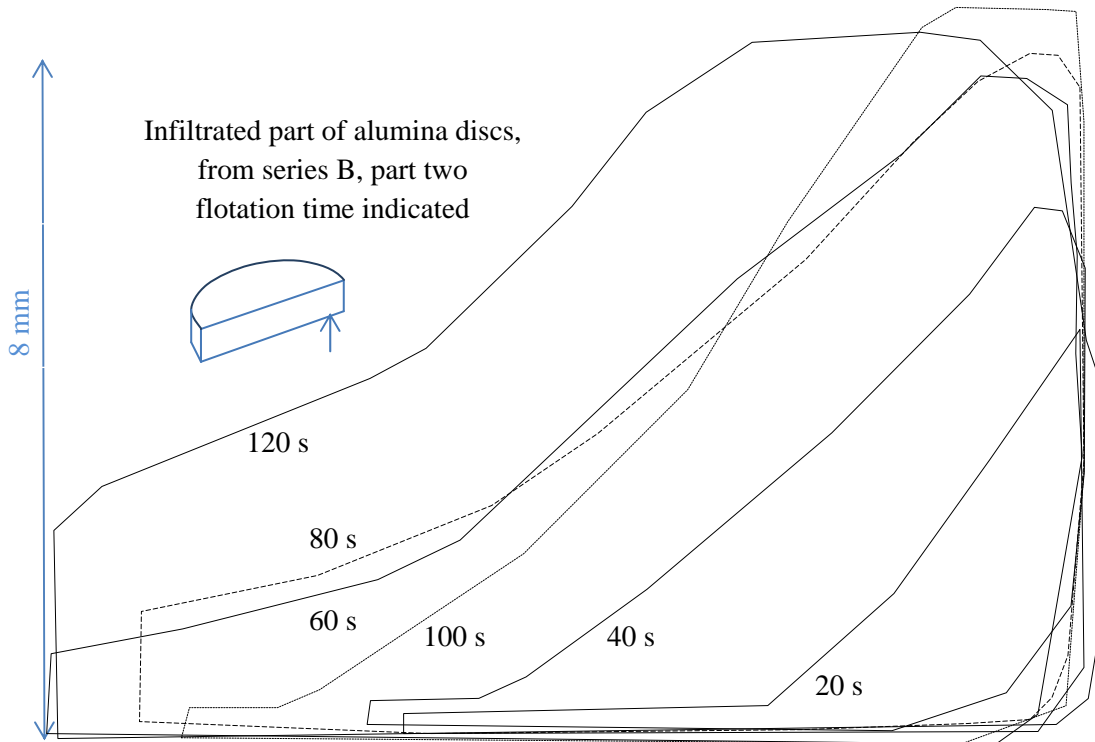
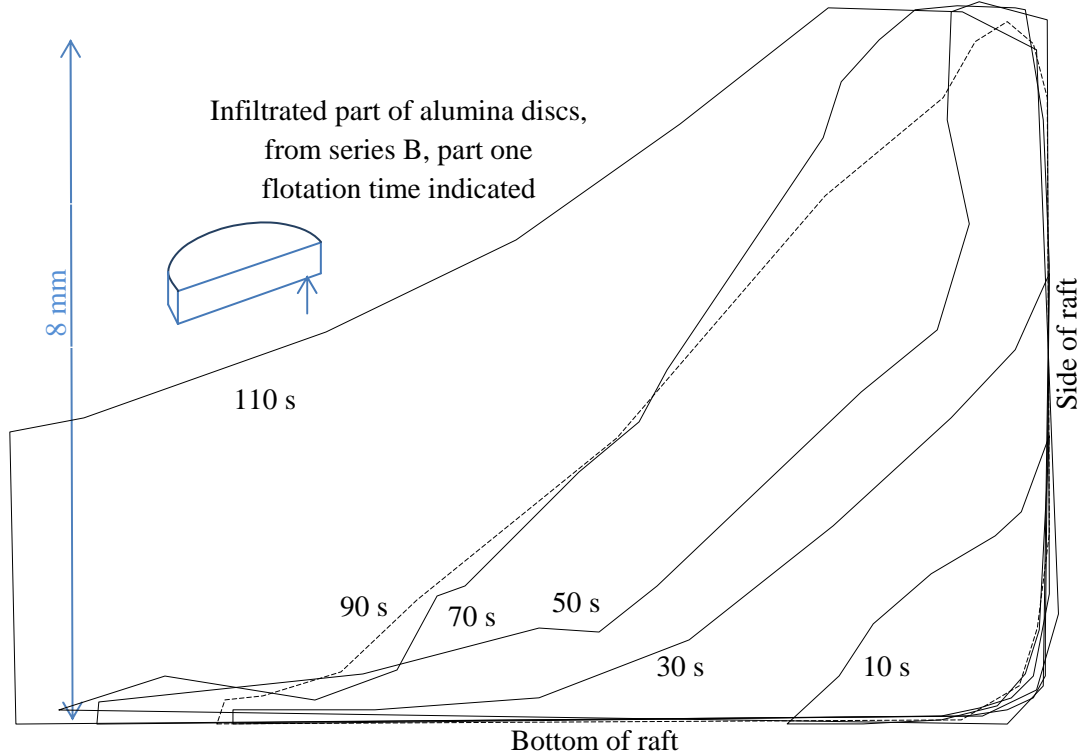


Figure 2. SEM image of alumina disc infiltrated by bath (sample upside-down) (series A, secondary alumina, 30 s).

Conducting a large set of experiments shows a clear general tendency of the

development of the infiltration. Although, the individual differences between the otherwise very similar alumina discs could alter infiltration (Figure 3.). It could have been due to slightly different compaction of the various-parts of a disc, a slightly thicker raft or maybe a rougher insertion. The slight fluctuation of the bath temperature, the superheat increasing with alumina content could contribute to the variations as well.



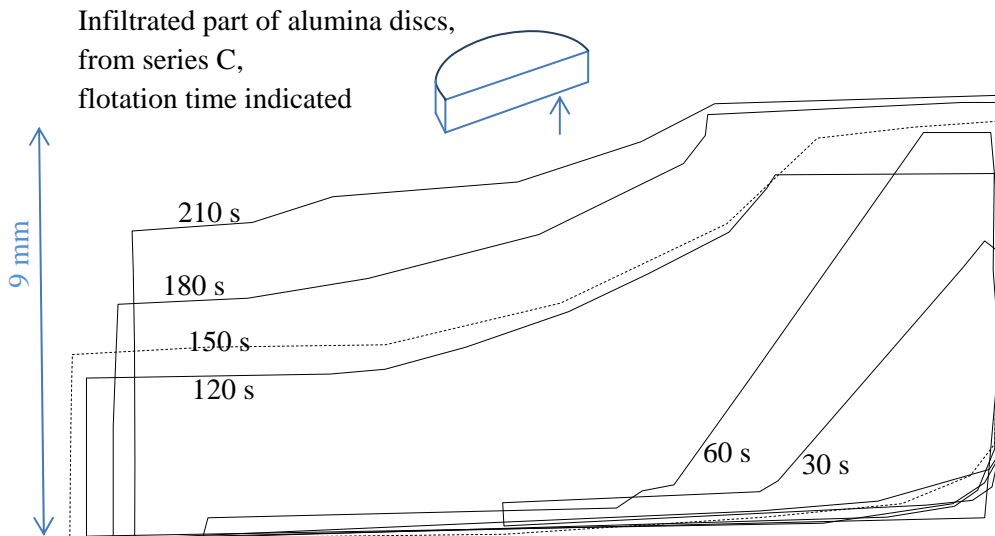


Figure 3. Infiltrated part of alumina discs (series B and C).

Since the corners of the discs were most exposed to the bath, they warmed up faster and that is where the infiltration started. The roundness of the corners could have come from the abrasion due to handling before insertion but also could be the result of dissolution. The fresh bath entered the discs from the corners; it could have dissolved some of the alumina and got saturated by the time it reached the middle of the disc. The front of infiltration gradually extended both horizontally and vertically. After around 50 seconds, the infiltration reached the maximum height around the edges.

It is important to note that although the infiltration reached the top of the disc in one minute of flotation time, the surface of the bath stayed on the edge of the disc, it did not flow over the wetted alumina even when the disc got soaked and the weight pulled it below the undisturbed bath surface, bending it downwards around the disc.

The flotation time of the discs left on the surface undisturbed until they sunk by themselves was about four minutes.

3.5. Mass and density of artificial rafts

The mass of the discs was weighted after they had been recovered from the bath and cooled down. After that, the unwetted part of the powder by the bath was removed, and the rest of the sample, namely the infiltrated zone together with the remaining frozen layer of bath (on the edges and under the bottom of the disc), was measured. Assuming that the initial mass of the discs was the average mass, the mass of the bath can be estimated (Figure 4).

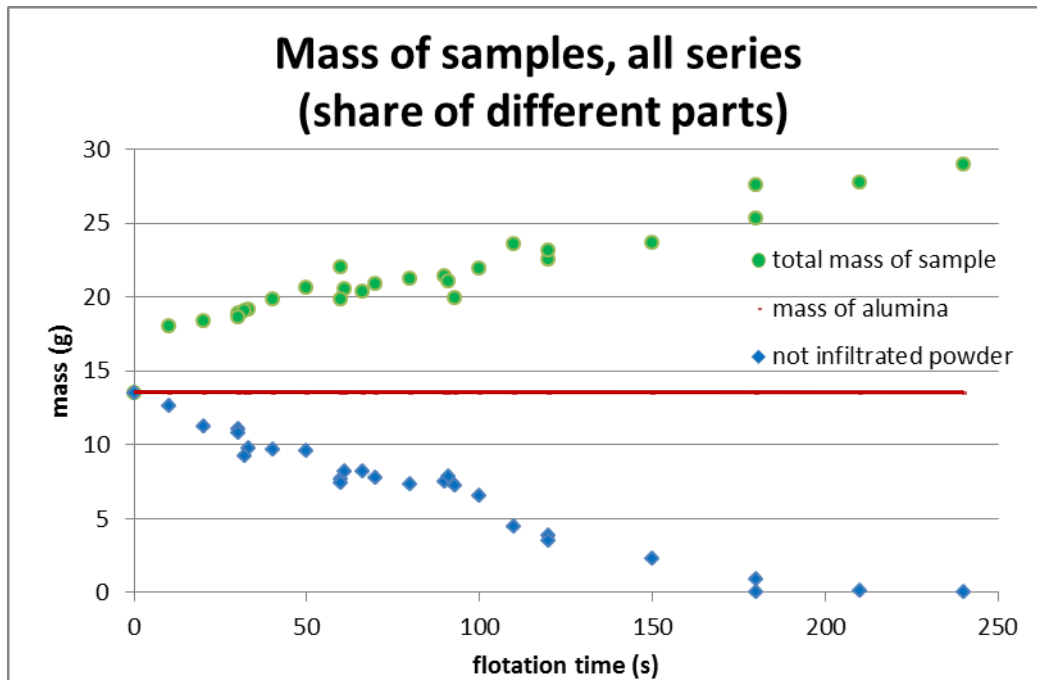


Figure 4. Progress of infiltration.

After an initial sudden increase of the mass due to the rapidly freezing bath, the mass growth was almost linear. The insertion resulted in the sudden solidification of the bath around the disc. Soon after that, the frozen layer started melting back rapidly while the infiltration began. Later, the infiltration front approached the center and at the same time, the porosity around the corners was decreasing, as it got soaked by the bath. Plotting the mass growth of the whole disc sample versus the mass of infiltrated powder, the correlation is more visible (Figure 5). By the time the alumina disc soaked up its own weight in bath, there was practically no non-wetted particle left. Theoretically the disc could take up twice as much bath if all of the gas would be replaced by the liquid but it did not reach that state during these experiments.

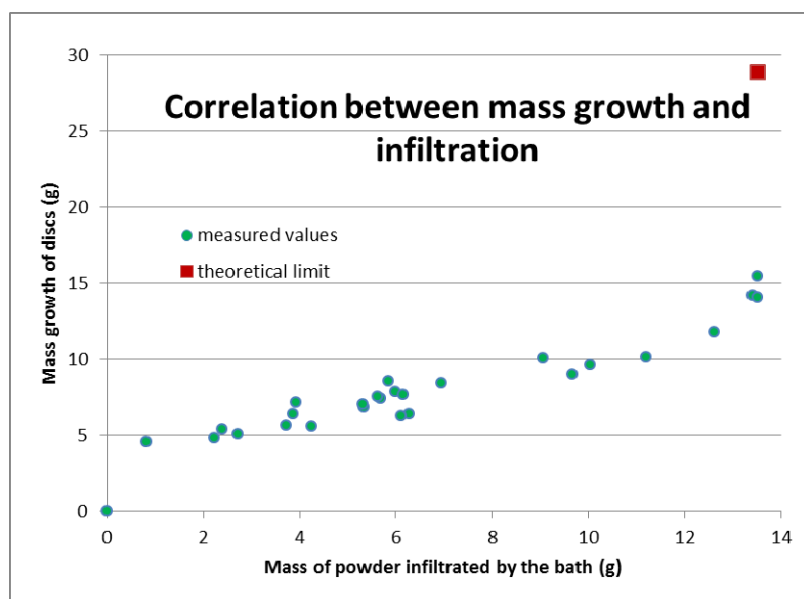


Figure 5. Correlation between mass growth of discs and infiltration.

Assuming that the volume of the discs did not change during the flotation and applying the average thickness of the alumina discs from our measurements, the density of the samples could be estimated (Figure 6). For comparison, the volume of the discs from series C was measured with the method of Archimedes. They were covered with hydrophobic silicon spray to avoid the contact with water.

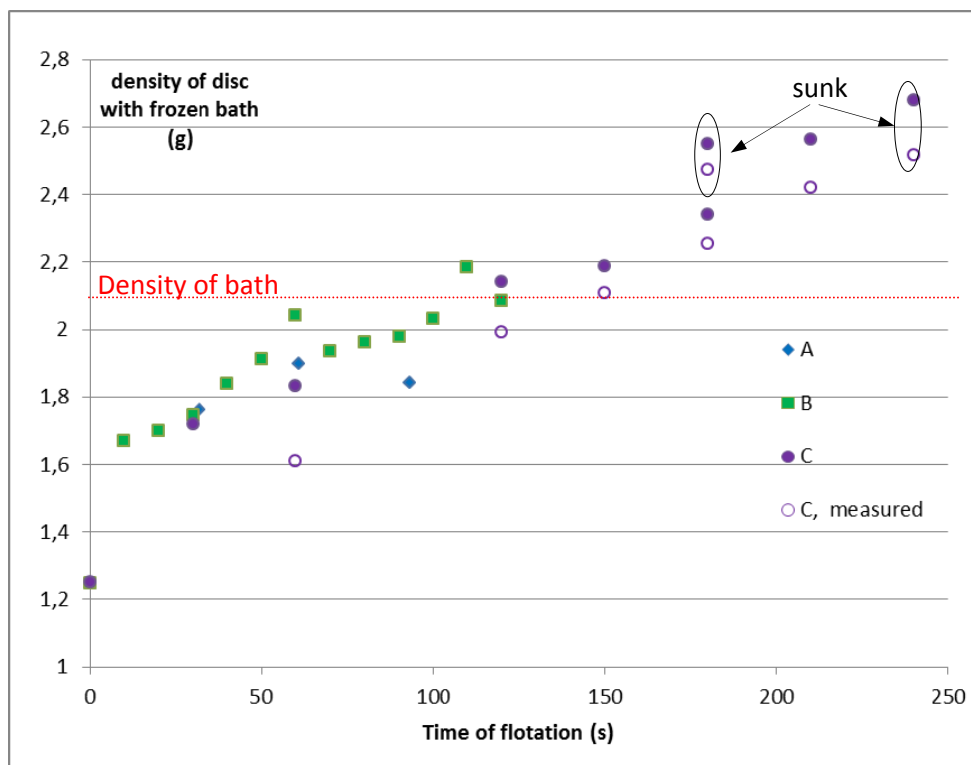


Figure 6. Density of samples, series A, B and C.

The density of the rafts reached the density of the bath after approximately two minutes and continued to increase. After that moment, beside the buoyancy, the surface tension kept the raft on the surface and flotation became sensitive to any disturbances. The curvature of the bath surface indicating the upward force of the surface tension was also well visible on the video recordings of the experiments.

4. Conclusions

Using compressed alumina discs as artificial rafts neglects the dynamic effects of the injection and provides slightly denser rafts, but it results in easily comparable samples and essentially the same physical and chemical processes take place in both the artificial and the real rafts. The biggest disadvantage of this method is that due to the closer placement of the particles, the sintering is stronger than it would be in a real raft and because of its homogeneity it would not break up on the surface as real rafts tend to at their weakest parts, where the powder compaction was looser. That being said - since the initial mass, density and geometrical form of these artificial rafts are known - they are excellent for the verification of models of the evolution of rafts, aiding the development of the model towards a more realistic representation, describing looser and more irregular rafts.

It was concluded by calculations, density measurements and visual observation that the raft could stay afloat after its density exceeded the density of the bath by more than 20 % and the surface tension played an important role in keeping it on the surface. Although the bath wets the alumina, the surface clung to the edge of the disc keeps it floating for up to four minutes. The effect of carbon particles and the significant amount of heat loss on the surface of the bath, resulting in the solidification of some of the bath around the edges of the discs, should be considered.

The sunken discs still contained some gas that was released soon after sinking.

5. Acknowledgements

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6. References

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