



Towards an Experimental Set-up for Measuring the Foaming Stability of Liquid Slags

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Abstract

The use of liquid bath furnaces has shown to be an energy efficient and environmentally friendly way for both the primary and secondary production of non-ferrous metals such as lead, nickel and copper. Typical for these kinds of furnaces is the injection or generation of reactive gasses which occurs below the surface of the liquefied feed material. The large amount of rising gases during processing can cause foaming of liquid slag. This slag phase is in most cases present as the upper layer of the liquid bath. The formation of excessive amounts of slag foam can hinder the production and lower the available capacity of existing smelting and converting furnaces. It is thus important to control this phenomenon and keep foaming to a minimum.

It is generally accepted that the formation of slag foam is caused by a combination of a large amount of rising gases and the inherent foam stability of the slag, which in turn depends on the physical properties of the liquid slag. The measurement of this foam stability can thus be an important tool in predicting and comparing the foaming behaviour of different slags.

In this work, a literature review is presented is the first step in the design of an experimental set-up for performing reliable measurements of the foaming stability of liquid slags at high temperatures, suitable for copper recycling and production. The simple model of Bikerman, on which the measurement of the foaming stability relies, is explained. In addition, the different suggested physical mechanisms for foam stabilization and breakdown are listed and the resulting influences of the physical properties of the liquid to the foaming stability are examined. It can be concluded that a general model



that fully explains the phenomenon of foaming does not yet exist and the need for a reliable method of measuring foaming stability of slags is high.

Introduction

This work summarizes the current status of recently started research on the foaming of slags during copper smelting. At the moment, focus is on a literature review which will be used as a starting point to get acquainted with the important influencing parameters and ultimately to design and build an experimental set-up to measure the foam stability of liquid slags in a reliable and repeatable way. Although further research will be focused on copper smelting slags, the designed set-up will also have its applicability for other types of slags.

Literature Review

Many production processes for both primary and secondary production of ferrous and non-ferrous metals involve the use of liquid bath furnaces. Inside these furnaces, feed material is first fully liquefied at temperatures between 1200 and 1600°C before reaction with a carefully chosen combination of reagents in order to achieve the desired products. These reagents can be gaseous, solid or even liquid. In many cases, these reagents are injected below the surface of the liquid bath using injection tuyeres or a submerged lance. Typically, this process leads to the formation of a liquid slag layer, which floats on top of the molten material. During processing, a significant amount of rising gasses in this liquid slag layer can occur. The origin of these gasses can be both from gas evolution during reaction or from gas injection below the liquid surface. These gasses rise to the surface of the liquid slag and can cause significant foaming under specific conditions. Generally, the formation of slag foam during production is an unwanted phenomenon since its presence limits the available capacity of existing furnaces and lowers the total efficiency of the process. The rapid and uncontrolled formation of large amounts of slag foam can even lead to slopping of the furnace in extreme situations[1], [2]. In these cases, foaming should be prevented as much as possible. In contrast, during steel production, while using an electric arc furnace (EAF), the formation of foam is desired to isolate furnace walls from the electrode hotspots, to sustain the electric arc and to keep heat losses to a minimum[3], [4]. In all cases, the prediction of the amount of slag foam is required to anticipate on its presence and keep the formation of slag foam under control.

In order to be able to predict and control the amount of slag foam present during metal production, extensive understanding is required on the mechanisms that lead to slag foaming and the parameters which influence this phenomenon. Especially the slag composition is considered to be an important parameter since it determines the slag chemistry and physical properties. Practically, a well substantiated relation is needed between the slag composition and its foaming characteristics that allows to predict which types of slags lead to extensive foaming and which do not. In this way, foaming can be considered during the design and the fine-tuning of a production slag for a specific process. This



approach includes the design of a method to quantify the foaming behaviour in order to be able to compare different slag compositions and investigate the influence of certain compounds.

It is generally accepted that the dynamic slag foam that is formed during processing, depends on two main factors: the total volumetric flow of rising gas bubbles and the inherent foam stability of the liquid slag. These influences are very intuitive and show that for foam to be formed, both rising gasses and a foam stabilizing liquid are required as is the case for soapy water at room temperature. At a fundamental level, it is believed that the formation of slag foam at high temperatures is governed by the same physical mechanism and principles as for water based foams at low temperatures[5]. It is for this reason that the phenomenon of slag foaming is often studied based on representative cold system experiments at room temperature[6], [7]. This avoids the many practical problems and difficulties that arise when performing high temperature experiments which involve liquid slags. Experiments to measure foaming stability mostly consist of a vertical tube in which the representative liquid or molten slag is present. Further, inert gas is injected at the bottom of the liquid at a known volumetric flow rate. This causes the liquid to separate in two distinct layers: a dispersed gas layer in which the injected gas bubbles rise freely and a foam layer which floats on top of the bubbly liquid. The thickness of the resulting foam layer at the surface of the liquid is measured while the volumetric flow rate of the injected gasses is varied. In this way, a relation can be established between the amount of rising gasses and the amount of foam. Two different set-ups of such a foaming experiment, which have been used by Hara[8] and Ogawa[7], are schematically shown in Figure 1. The two set-ups differ in how the gasses are injected at the bottom of the liquid bath. Foaming experiments in the past, both at low and high temperatures, have led to a few models that attempt to describe the phenomenon of foaming.

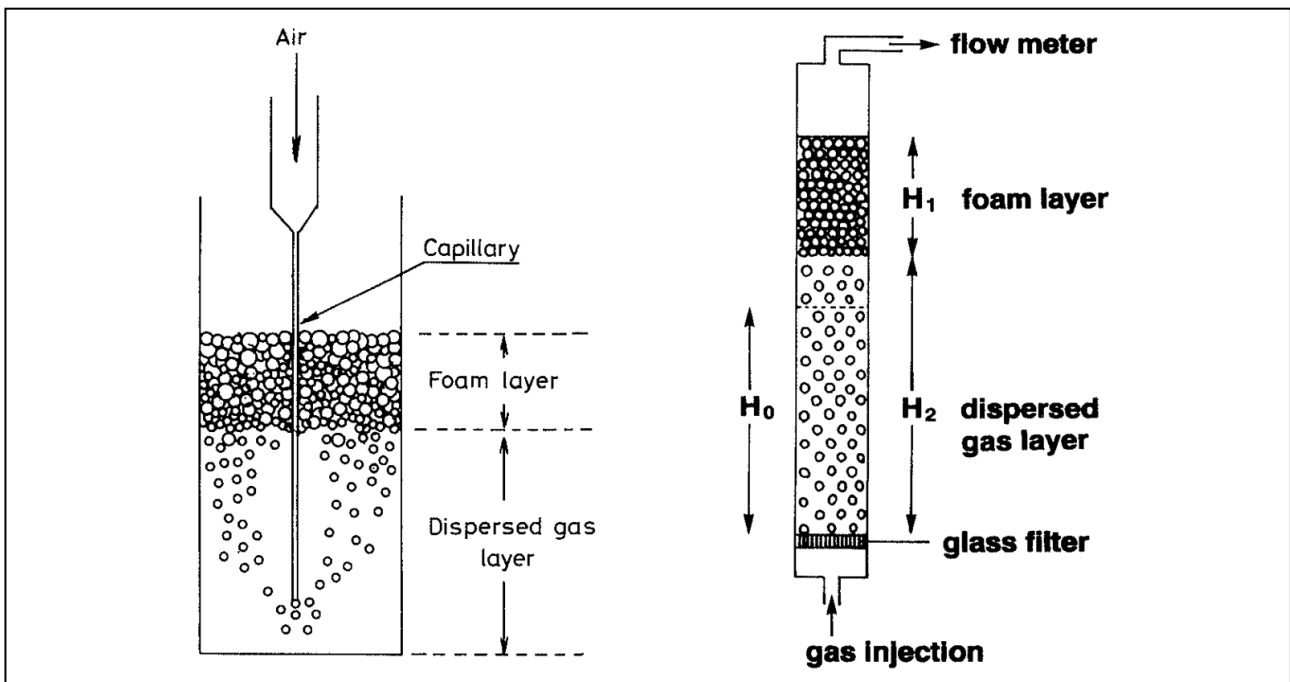


Figure 1: Schematic figure of two possible setups for performing foam stability measurements, used in literature: left[8], right[7].



Bikerman's model of dynamic foaming

The most simple, but still the most used, model to predict foam volumes due to freely rising gas bubbles was suggested by Bikerman[9]. He stated that the volume of foam V on top of the liquid slag layer is linearly related to the volumetric flow of rising gasses Q_g as is shown in equation (1):

$$V = Q_g \Sigma \quad (1)$$

Σ is the Bikerman constant or foaming index and relates the two previously mentioned quantities. The foaming index has the dimension of time and acts as a quantity that expresses the inherent foaming stability of the foam forming liquid. Equation (1) relates the amount of rising gasses and the foam stability of the liquid to the volume of dynamic foam, present on top of the liquid. It also shows that both rising gasses and a liquid with sufficient foam stability are required in order to sustain a significant amount of foam. The foaming index Σ , or foaming stability, is thought to exclusively depend on the physical properties of the liquid, such as viscosity, density and surface tension but it is shown in cold experiments that the bubble size distributions of the rising gasses also have a significant influence on the value of this index. Small bubbles tend to cause much more stable foams than large bubbles[1], [10]–[12].

The foam here is said to be dynamic since the amount of foam at a certain point in time is given by the balance between the formation rate of foam at the liquid surface, due to rising bubbles, and the rupture rate of foam at the top of the foamy layer. The change in volume can thus be expressed as the difference between these two rates as can be seen in equation (2):

$$\frac{dV}{dt} = Q_{\text{gen}} - Q_{\text{rup}} \quad (2)$$

Here are Q_{gen} and Q_{rup} the volumetric generation and rupture rates of the present foam, respectively. The foam formation rate is related to the total volumetric flow of the rising gas bubbles Q_g since all gas bubbles are trapped in the foam layer. The foam volume that is formed from a certain volume of gas can be calculated using the void fraction α of the foam which is the volume fraction of foam that consists out of gas. The rupture rate of the foam is assumed to depend linearly on the total volume of foam V , coupled by a certain time constant τ which represents the foam lifetime[10]. In this way, the volumetric flow rates in equation (2) can be written explicitly as shown in equation (3):

$$\frac{dV}{dt} = \frac{Q_g}{\alpha} - \frac{V}{\tau} \quad (3)$$

We can use the differential equation in equation (3) to calculate the equilibrium volume of foam by choosing the time differential of the foam volume V to be zero. The equilibrium volume of foam can thus be expressed as can be seen in equation (4):

$$V = Q_g \frac{\tau}{\alpha} \quad (4)$$

For general foams, the void fraction α is close to unity[13]. By comparing equation (1) and equation (4), it can thus be concluded that τ and Σ are approximately equal for general foams. The foaming



index represents the characteristic time of spontaneous foam breakdown and is thus a direct quantity to describe inherent foaming stability of a liquid. Because of the dynamic nature of the foam layer, the foaming index is sometimes referred to as the residence time of the gas bubbles in the foam layer. Bubbles join the foam structure at the liquid-foam interface and travel upwards through the foam layer due to buoyancy until they eventually rupture at the top of the foam. The foaming index or residence time is thus the characteristic time required for a certain gas bubble to travel through the entire foam layer.

It has to be noticed that linear relation between the volumetric flow rate of rising gasses Q_g and the dynamic volume of foam V as described by the Bikerman relation in equation (1), is subject to a number of restrictions. Most importantly, the model is only valid for foam, formed by freely rising gas bubbles. This means that there always has to be a dispersed gas layer present under the foam layer in which the injected gas bubbles can rise exclusively due to buoyancy. At high flow rates of injected gasses, such a large amount of foam can be generated that the liquid bath beneath the foam gets depleted completely. Increasing the gas flow even more causes gas to be directly injected into the foam layer. This will cause rapid rupture and an increased instability of the foam. This is clearly seen during foaming experiments conducted by Wu et al.[14] They observed a significant decrease in foam stability at high gas flow rates after the whole liquid bath was converted into foam. In order to be able to generate a large enough range of foam volumes, the volume of the initial liquid bath should thus be significantly large.

Mechanisms for foam formation and breakdown

To get a better idea of which parameters influence the foam stability of a liquid, the suggested mechanisms of foam formation and breakdown are summarized. Foam is formed due to the large amount of rising gas bubbles that join the foam structure at the liquid/foam interface. The fresh layers of foam bubbles get pushed out of the liquid due to the buoyancy of new incoming bubbles. The liquid trapped in the lamellae between the bubbles is then carried upwards. While the foam structure rises due to buoyancy, the liquid between the bubbles start to drain back towards the liquid bath beneath the foam layer due to gravity. The process is slowed down by the viscosity of the liquid. This drainage causes the void fraction of the foam to increase and the thickness of lamellae in between the gas bubbles to decrease. During this process, the foam structure consisting of spherical gas bubbles with thick lamellae changes to a structure which exists out of polygonal gas bubbles, separated by thin lamellae. This process is sometimes also called the transition from wet to dry foam due to drainage. It is believed that the bubbles in the foam stay stable until the thickness of the liquid walls drops below a critical value which causes the film to rupture instantly due to the surface tension of the liquid[15]. Bubbles in the upper layers of the foams are expected to rupture the most since they are the oldest and have had the most time to get the liquid drained from in between them. This mechanism of drainage suggests that both viscosity and density of the liquid have a clear influence to the stability of foam and thus influence the foaming index directly. A higher viscosity should increase the foaming index, or foam lifetime, while a higher density should lower the foaming index[13].

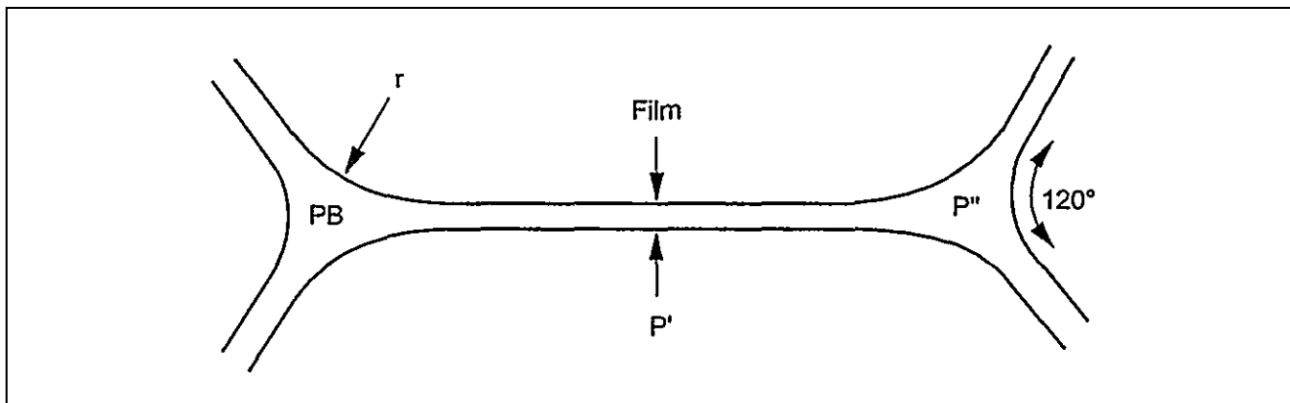


Figure 2: Illustration of plateau border suction. Liquid is pushed towards the plateau border (PB) due to a pressure difference between P' and P'' caused by the curvature r . [16]

When the foam structure changes from spherical to polygonal, the bubbles get deformed from their equilibrium spherical shape. This causes a pressure difference to be established between the centres of the liquid lamellae (P'), where the curvature is low, and the intersections at which the lamellae come together (P''), where the curvature is high. These places where multiple lamellae come together in a line, are called plateau borders. This effect is thus called plateau border suction and is illustrated in Figure 2. Plateau border suction causes liquid to be sucked away from the lamellae to the plateau borders [16], [17]. This surface tension driven effect thins the lamellae and thus aids film rupture. On the other hand, the surface tension is also thought to increase the foam lifetime due to the Marangoni effect and capillary forces. The latter is clearly shown during foaming experiments in micro-gravity environments [18], [19]. It was observed that, in the absence of gravity, liquid can be sucked back into the foam lamellae due to capillary forces and in this way re-wet dry foam to be transformed back into wet foam. This effect, called foam humidification, clearly counteracts the drainage due to gravity.

The Marangoni effect is also thought to stabilize existing foam and promote foam formation in solutions containing surfactants. This effect differs from the previous explained effects since the Marangoni effect requires a surface active component to be present in the foaming liquid. When a liquid film, saturated by a surfactant at its surface, is stretched, a restoring force is observed. This force is caused by the dilution of the surfactant at the film surface when the surface is expanded. The increase in free energy that is accompanied with this dilution is observed as a surface contracting force and is proportional to the strain of the surface. The matching surface modulus is called the Marangoni modulus and depends strongly on the strain rate of the surface. This is because the dilution of the surfactants is also counteracted by the diffusion of surface active compounds from the bulk of the film to its surface. Fast deformation thus suffers the largest restoring forces since diffusion can be neglected at small timescales. Slow deformation, on the other hand, suffers from lower restoring forces since a part of the diluted surfactant is replaced by diffusion. The exact influence of the Marangoni effect on the stability of foam still remains unclear. It is observed during cold foaming experiments that the amount of surfactant in the liquid has a significant effect on its foam stability [6], [8], [20]. Even small amounts of surface active compounds can cause a large increase in the stability of the foam as can be seen by comparing the foaming stability of pure water and a water/soap mixture. This stabilization is



thought to be caused by the fixation of the liquid/gas interfaces due to the Marangoni effect and in this way provide a rigid skeleton of interfaces from which liquid drains due to gravity.

Due to the multiple suggested mechanisms, such as plateau border suction, capillary forces and Marangoni flow and elasticity, caused by the surface tension related phenomenon, it is hard to point out the overall effect of the surface tension on the foam stability. Generally, it is observed that by adding surface energy lowering compounds, the foaming stability can be increased drastically but it is unclear if this effect is due to the general lowering of the surface tension or due to the mechanisms related to the surface active properties of the added compound.

Surface active compounds can have an additional effect. When the two surfaces of a thin liquid film contain surface active compounds which induce surface polarization, a repulsive force can be present between the two interfaces. This force acts at a very short range (<100nm) but can cause the foam stability to increase drastically for foams with a critical film thickness smaller than the distance over which the thin-film interaction reaches[21]. The film is thus prevented from reaching its critical thickness for rupture due to repulsive forces between the interfaces. The critical thickness for water films, for example, can be less than 10 nm[15]. When undisturbed, these foams can be retained for very long periods of time and will eventually collapse due to alternative mechanisms such as bubble coalescence and Oswald ripening. Foams stabilised by this repulsive force between surfaces are called thin-film interaction stabilised. These foams are sometimes called metastable and can have very large lifetimes when left undisturbed. They differ significantly from other foams which do not show this behaviour. The latter type is called viscoelastic stabilized foams. These foams can also have long lifetimes due to the slow rate of foam drainage but will always be inherently unstable.

Prediction of the foaming index of liquid slags

In the past, efforts have been made to measure the foaming index of various slags with different compositions, almost all related to iron and steel production processes[10], [11], [22]. These foaming indices are afterwards related to the physical properties of the slags which influence the foaming behavior as is predicted by the previously stated foaming mechanisms. This relation is constructed, based on a dimensional analysis of the experimentally measured foaming indices and liquid properties. The most frequently found relation is shown in equation (5):

$$\Sigma \sim \frac{\mu}{\sqrt{\gamma\rho}} \quad (5)$$

In equation (5), μ is the dynamic viscosity of the liquid slag, γ the surface tension and ρ the density. The fit of the experimentally gathered data to the previously stated relation is generally poor. This is most likely due to the difficulty of accurately and repeatably measuring the foaming indices and physical properties of liquid slags. In the past, many more relations than the one shown in equation (5) have been suggested.



Low-temperature experiments have been conducted in order to try to simulate the foaming behavior of liquid slags. It is believed that liquid slag foams do not exhibit thin-film interactions in their lamellae or that the critical thickness for rupture of the liquid slag film is significantly larger than the thickness at which this phenomenon occurs. Slag films are reported to rupture at thicknesses around 50 μm [23]. Far above the thickness of approximately 100 nm at which thin-film interactions become significant. Slag foam is thus expected to be stabilized by viscoelastic forces only. Comparing low-temperature foams with liquid slag foams should thus be only valid when these low-temperature foams show the same rupture behavior. Ghag et al.[23] performed foaming experiments on such cold systems in order to compare with available data of slag foaming. They used a water/glycerol mixture of different compositions to vary the viscosity of the liquid and added a surface active compound in order to vary the surface tension. During the experiment, the influence of the average bubble size was also investigated, something which is very challenging during high-temperature experiments. The derived relation between foaming stability and liquid properties differs significantly from the most frequently found relation for high-temperature slag foaming. The use of the surface tension itself did not lead to a relation with adequate accuracy. A much better fit to the experimental data was found when the effective Marangoni modulus was used instead of the surface tension. This Marangoni modulus was corrected for the applied strain rate. Also, the average bubble diameter turned out to be of a major influence. The relation, derived by Ghag et al.[23] is shown in equation (6).

$$\Sigma \sim \frac{\mu E_{\text{eff}}}{\rho^2 d^3} \quad (6)$$

In equation (6), μ is the dynamic viscosity of the liquid slag, E_{eff} the effective Marangoni modulus, ρ the density and d the average diameter of the gas bubbles. This equation provides a good relation between liquid properties and the foaming index of the studied system, especially when compared with similar relations, derived for liquid slag systems. This can be attributed to the ease of measuring liquid properties and the performance of foaming experiments at low temperatures, compared to measurements and experiments using liquid slags.

Conclusion

During this study, it became clear that experiments show differences in the relation between the foaming stability and physical properties for liquids at low and high temperatures. Even between different slag systems at high temperatures, different relations were found. This difference is unexpected since the physical foaming mechanisms are assumed to be equal at low or high temperatures for viscoelastic stabilized foams. The observed differences can at the moment be attributed to the difficulty of performing reliable and repeatable foaming experiments using liquid slags. Moreover, accurate values for viscosity and surface tension are not available for many of the used slag compositions. This makes it very hard to link the inherent foaming stability or foaming index of a liquid slag to its physical properties. Additionally, foaming is a very complex phenomenon in which the contribution and interaction of the different possible mechanisms are still unknown. Further research is required to better understand and predict the formation of slag foam.



A first step in the future work would be to design a reliable experimental set-up to measure foaming indices of multiple compositions of liquid slags in an accurate and reproducible way. A well-designed and documented experimental set-up like this is currently not available according to literature. Then, the foaming index of a resembling cold liquid system should be measured in a geometrical equivalent set-up. By comparing the foaming behaviour of the liquid slag system and the resembling cold liquid, the hypothesis of equal physical mechanisms can be tested and further insights can be gained regarding the differences and similarities between hot and cold foaming liquids. Such set-ups are currently under design. The geometry of the set-up is being optimized using low-temperature foaming experiments. Special attention is given here to the way gasses are injected in the liquid bath, since the injection directly influences the size of the generated bubbles. This bubble size distribution was already shown to be of significant importance. The materials, used for the construction of the high-temperature slag foaming experiments, will be selected based on erosion experiments involving liquid slags at operation temperatures. In this way, an optimal experimental set-up can be designed to provide new insights in the complex phenomenon of slag foaming in pyrometallurgical processes.

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