

FEDERAL UNIVERSITY OF SÃO CARLOS
CENTER FOR EXACT SCIENCES AND TECHNOLOGY
GRADUATE PROGRAM IN MATERIALS SCIENCE AND ENGINEERING

**FUNDAMENTAL ASPECTS AND TECHNOLOGICAL APPLICATIONS
OF BUBBLING FOR NON-METALLIC INCLUSION REMOVAL AND SLAG
FOAMING IN STEELMAKING**

Luís Otávio Zaparoli Falsetti

São Carlos-SP
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Luís Otávio Zaparoli Falsetti

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DEDICATION

*To the young kid, who once aspired to be a scientist,
and to each and all who supported his journey.*

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ABSTRACT

Bubbles are applied in a wide range of industrial processes, such as ore flotation, aluminium foaming and even texture control in foods. In steelmaking, gas bubbles are typically injected into the liquid steel to remove non-metallic inclusions and into the slag to induce its foaming in the electric arc furnace (EAF). Currently, challenges in the steel industry are driven by both the sector's sustainability and the demand for steels with improved properties, particularly in achieving greener and cleaner steels. EAF slag foaming and non-metallic inclusion removal using bubbling through porous ceramic plugs are closely linked to these challenges and can benefit from a better understanding of the fundamentals involved in the use of gas bubbles. Therefore, this doctoral thesis investigates the fundamental mechanisms and technological applications of gas bubbling in steelmaking, specifically targeting the removal of non-metallic inclusions and the control of slag foaming. The study is divided into three main approaches: bubble generation, inclusion flotation kinetics, and slag foam stability. First, the influence of the purging plug's surface wettability on bubble size was modelled, establishing a combined model that delineates pore-dominated and material-dominated bubbling regimes. It was demonstrated that although non-wetting ceramic surfaces prevent liquid steel infiltration, they generate bubbles larger than 10 mm, which are less effective at removing inclusions. Second, physical simulations in a tundish water model evaluated the flotation of hydrophobic and hydrophilic particles. The results identified a trade-off where smaller bubbles (0.6 mm) achieved higher removal efficiencies, but slower removal rates than larger bubbles (1.1 mm). Finally, a framework coupling computational thermodynamics (FactSage) and machine learning (GlassNet) was developed to predict slag foamability. This framework was applied to investigate defoaming agents, identifying a by-product of the continuous casting as a potential alternative to fluorine-based additives for accelerating foam collapse by reducing the slag's effective viscosity.

Keywords: non-metallic inclusion; purging plug; slag foaming; smart bubbles; steelmaking.

RESUMO

ASPECTOS FUNDAMENTAIS E APLICAÇÕES TECNOLÓGICAS DO BORBULHAMENTO NA REMOÇÃO DE INCLUSÕES NÃO METÁLICAS E NA ESPUMAÇÃO DE ESCÓRIAS EM ACIARIA

O uso de bolhas ocorre em uma ampla gama de processos industriais, tais como a flotação de minérios, a espumação de alumínio e até mesmo o controle da textura em alimentos. Na aciaria, bolhas de gás são tipicamente injetadas no aço líquido para a remoção de inclusões não metálicas e, na escória, para induzir a espumação no forno elétrico a arco (EAF), processos cruciais para a produção de aços mais limpos e sustentáveis. Atualmente, os desafios da indústria siderúrgica são impulsionados tanto pela sustentabilidade do setor quanto pela demanda por aços com propriedades aprimoradas. Esta tese de doutorado investiga os aspectos fundamentais e as aplicações tecnológicas do borbulhamento visando a otimização destas etapas. O estudo está dividido em três abordagens principais: geração de bolhas, cinética de flotação de inclusões e estabilidade da espuma de escória. Primeiramente, modelou-se a influência da molhabilidade superficial do plugue poroso no tamanho da bolha, estabelecendo-se um modelo combinado que evidencia os regimes de borbulhamento definidos pelos poros e pelo material. Demonstrou-se que, embora composições cerâmicas de baixo molhamento previnam a infiltração de aço líquido, elas geram bolhas maiores que 10 mm, que são menos eficazes na remoção de inclusões. Em segundo lugar, simulações físicas em um modelo em água de distribuidor avaliaram a flotação de partículas hidrofóbicas e hidrofílicas. Os resultados identificaram um compromisso, dado que bolhas menores (0,6 mm) resultam em maiores eficiências de remoção, porém, com taxas de remoção mais lentas em comparação com bolhas maiores (1,1 mm). Por fim, uma rotina acoplada entre termodinâmica computacional (FactSage) e aprendizado de máquina (GlassNet) foi desenvolvida para prever a espumabilidade da escória. Essa rotina foi aplicada para investigar aditivos de desespumação, identificando um subproduto do lingotamento

contínuo como uma alternativa àqueles contendo flúor, acelerando o colapso da espuma pela redução da viscosidade efetiva da escória.

Palavras-chave: inclusão não metálica; plugue poroso; espumação de escória; bolhas inteligentes; aciaria.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

AD	Air Diffusers
ASTM	American Society for Testing and Materials
BOF	Basic Oxygen Furnace
DABuT	Delft Argon Bubbling Tundish (Specific water model facility)
DRI	Direct Reduced Iron
EAF	Electric Arc Furnace
EDS	Energy Dispersive X-Ray Spectroscopy
HBI	Hot Briquetted Iron
ISD	Isothermal Solubility Diagram
LF	Ladle Furnace
NMI	Non-Metallic Inclusion
PB	Porous Brick
PE	Polyethylene
PMMA	Polymethyl methacrylate
SEM	Scanning Electron Microscope
VD	Vacuum Degasser
XRD	X-Ray Diffraction

Latin symbols

A	Area of bubbler surface (cross-section)
A _{BB}	Modified Hamaker constant
B ₂	Binary basicity (CaO/SiO ₂ ratio)
C _B	Bubble base circumference
D _B	Bubble diameter (or equivalent diameter)
D _O	Orifice/pore inner diameter
D _{No}	Nozzle outer diameter
D _P	Particle diameter
E _B	Bubble energy (growing in bubbler)
E _{eff}	Effective elasticity

Eff	Maximum efficiency (flotation)
Eo	Eötvös number
F _b	Buoyancy force
F _σ	Surface tension force (Force component)
F	Solid fraction in volume
Fr	Froude number
g	Gravitational acceleration
h _{foam}	Height of sustained foam
I	Light intensity
P	Pressure
P _A	Probability of adhesion
P _C	Probability of collision
P _D	Probability of detachment
Q _g	Gas flow rate
Q _{t_n}	Ratio of specific ageing times (fractional change)
R _B	Radius of the bubble's spherical cap
Re	Reynolds number
t	Time
t _{cl}	Specific time for coalescence
t _{cs}	Specific time for coarsening
t _{dn}	Specific time for drainage
T	Temperature
TS	Time Scale (flotation decay)
U _g	Superficial/linear gas velocity (L/min/m ²)
V _B	Bubble volume
V _r	Terminal/rising velocity of a particle

Greek symbols

α	Interaction factor (Einstein-Roscoe equation)
γ	Surface or interfacial tension
ΔE	Energy barrier - subscripts 'a' for attachment, 'd' for detachment
θ	Contact angle

λ	Scale factor (between model and prototype)
μ	Dynamic viscosity
μ_{eff}	Effective viscosity
ρ	Density
Σ	Foaming Index
σ	Surface or interfacial tension

CHAPTER 1 – INTRODUCTION

Historically, liquid iron processing finds strong archaeological evidence in China and India around 200 B.C., with the accidental discovery of the blast furnace and its development occurring near the end of the Middle Ages. Furthermore, the emergence of iron ore reduction processes is associated with the Hittites, a people who inhabited Anatolia (modern-day Turkey), around 2000 B.C. Although iron utensils are found in excavations predating these dates, they are associated with meteoric sources rather than ore reduction by human labour. Much of the development of the steelmaking process occurred accidentally and continuously, though the first disruptive development in steelmaking was the invention of the Bessemer converter in the 1850s, which allowed steel to be obtained from pig iron by oxygen blowing, as represented in Figure 1.1 (1).

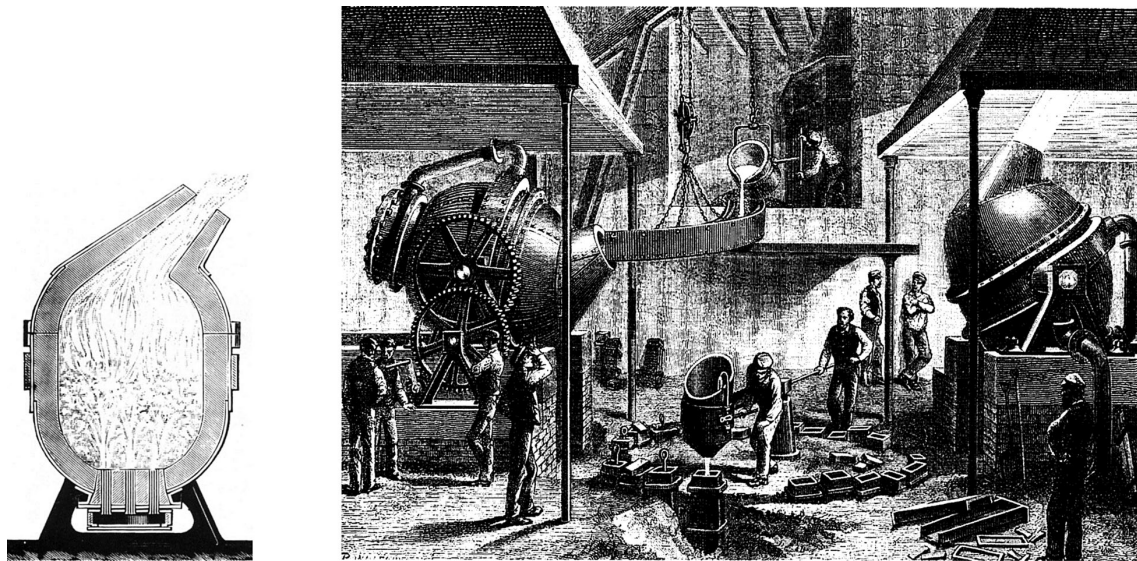
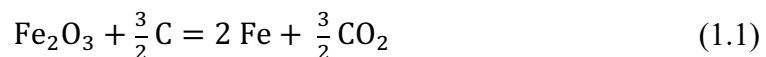


Figure 1.1: The Bessemer converter (left) and the Bessemer's steelworks at Sheffield after 1859 (1).

Oxygen injection in the Bessemer converter allowed for greater control of silicon and carbon composition in the produced steel. The process was subsequently modified to promote steel deoxidation through the addition of manganese sources. In this sense, concern for the final composition of the produced steel motivated subsequent technologies added to the steelmaking process, looking for (2):

- Control of hydrogen, nitrogen and oxygen contents in liquid steel, as well as the formation of non-metallic inclusions;
- Induce desulfurization and dephosphorization of the metallic bath;
- Reduce carbon contents to ppm levels, while avoiding the oxidation of other alloying elements.

Although steelmaking is currently facing an optimisation and maturation of its industrial processes to meet compositional requirements, it is evident that its main challenge currently lies in reducing the carbon footprint, given that the sector is responsible for 7% of annual CO₂ emissions (3). This high share is based on the principle of iron ore reduction production in the blast furnace, which uses the reaction with carbon (coke, charcoal, etc.) to obtain the metal, according to Equation (1.1) (4).



Analysing this reaction, it is noted that the products - 2 moles of Fe (or 112 g) and 1.5 moles of CO₂ (or 66 g) - generate at least 600 kg of CO₂ for every ton of steel produced by reduction via carbon, without even considering the reactor efficiency and auxiliary processes based on external heating. In practice, this value is around 1.77 tons of CO₂ per ton of pig iron for the blast furnace-oxygen converter route, showing that the sector's decarbonization depends not only on a new reduction route via hydrogen but also on greater energy efficiency (5).

In addition to the significant challenge of decarbonization, which is not exclusive to this sector, steelmaking also faces demands related to (6):

- The availability and quality of raw materials, whether iron ore for reduction or metallic scrap for melting;
- The high energy consumption for scrap melting in the electric furnace, associated with an efficiency close to 55%, mainly due to thermal losses from exhaust gases;
- The volume of slag and other by-products generated during iron and steel production, demanding the disposal of 400 - 800 kg of material per ton of liquid steel;

- The demand for clean steels, i.e., with lower inclusion levels (oxygen below 10 ppm), to meet the automotive and aerospace industries.

Among the challenges proposed to current steelmaking, increasing energy efficiency and producing clean steels are interrelated in a not-so-explicit way: in gas bubble engineering. The migration to hydrogen-based iron ore reduction requires a steel refining route in the electric arc furnace (EAF) (4). In this reactor, a large share of low energy efficiency comes from the heat radiated by the arc, which is not employed to heat the metallic bath. By foaming the slag, the graphite electrode is covered by this phase, the arc energy is transferred to the slag and, consequently, to the metallic bath. In numbers, this causes the average energy efficiency to go from 36% to 93% (7). Further along in the process, steel deoxidation occurs by adding oxidising alloying elements (such as Al, Si, Mn), so that non-metallic inclusions, typically oxides, are precipitated in the metallic bath. Thus, the main process for removing such solids occurs through inert gas bubbling in the ladle or tundish, transporting the phase to the slag (8).

In this way, slag foaming in the electric furnace and the removal of non-metallic inclusions in secondary refining are processes that illustrate the importance of using bubbles in the melt shop, allowing for the production of greener and cleaner steels. Therefore, this doctoral thesis addresses the understanding of the fundamentals involved in the application of bubbles as the central problem to be studied, breaking it down into the following objectives (and respective chapters):

- Correlate pore size and chemical composition of the bubbler (porous plug) with the generated bubble size, comparing it with the ideal diameter to maximise inclusion removal (Chapter 2);
- Investigate the effect of bubble size and gas flow rate on the kinetics of suspended particle removal, using a physical model that reproduces the behaviour of inclusions in the tundish, a steelmaking reactor (Chapters 3 and 4);
- Study how bubble ageing mechanisms apply to foaming slags and predict the effect of chemical composition on the stability of the foam covering the electrode and being poured from the furnace (Chapters 5 and 6).

CHAPTER 2 – BUBBLE GENERATION IN REFRACTORY POROUS PLUGS: THE ROLE OF THE CERAMIC SURFACE COMPOSITION

2.1 Introduction

Having in mind the role of inert gas bubbles to withdraw inclusions from the molten bath, the current chapter addresses the influence of pore size and surface wettability on the generated bubble diameter. To improve purging plug performance, the goal is a plume of bubbles within an optimised range, reported in the literature as 1 to 5 mm. However, experimental challenges are typically faced in measuring the size of a bubble in liquid metal. Thus, this work calculated the bubble size based on force equilibria, determining the point at which the bubble detaches from the surface in the quasi-static regime. This approach defines a lower size limit to the generated bubble, as the dynamic regime (e.g., at higher gas flow rates) can increase it. The obtained values were compared to experimental data for a water-based system, and the model was extrapolated to understand the bubble generation by porous surfaces in contact with molten steel.

2.2 Literature review

Non-metallic ceramic inclusions, typically consisting of oxides and sulphides, act as defects in the metallic matrix and can spoil their mechanical properties (9,10). The level of tolerance for inclusions in the steel is determined by its processing step and the final application, as the main target is to attain a “clean steel” (11,12). These inclusions have many origins throughout steelmaking and can be classified accordingly. The exogenous ones come from fragments of refractories or entrapped slag, whereas the reaction among the steel constituents within the molten bath may generate endogenous inclusions (13). A method to remove these particles from the liquid steel is to inject argon gas into the ladle via a ceramic plug (as in Figure 2.1), a refractory product installed at the bottom of the steel ladle, which contains either interconnected open pores or straight slits (14). The interaction between the generated bubbles and the ceramic particles takes place by two different mechanisms, whereby non-metallic inclusions are withdrawn to the slag phase: (i) by attaching the ceramic particle to the bubble’s surface or (ii) by a

plain kinetic mechanism, in which the particle is captured by the bubble wake flow (15). Thus, the metallurgical challenge of producing clean steels can be translated into an opportunity to design both refractory linings with low corrosion wear rates and ceramic plugs that generate ideal bubbles to capture inclusions.

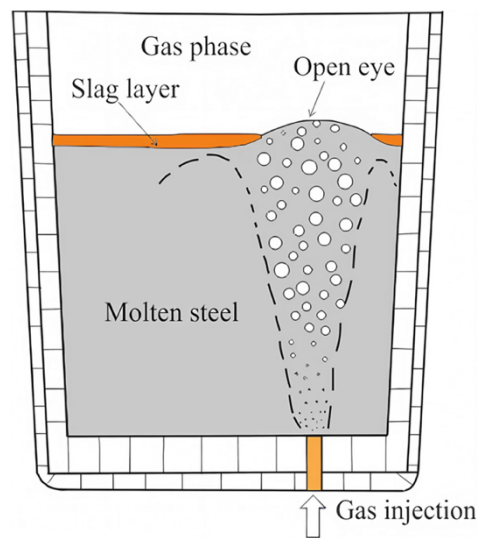


Figure 2.1: Schematic representation of gas injection into the steel ladle (16).

Bubble generation in liquid media takes place in several unit operations, which comprise interfacial interaction between two or more phases. As the optimum range of bubble sizes is inherent to a specific process and defined by the thermodynamic and kinetic aspects (17), understanding the mechanism of bubble generation turns out to be a key factor to maximise its efficiency. Experimental simulations in aqueous media, simplified by a low temperature and the transparency of the liquid, provide laboratory-scale tests to study the influence of intrinsic factors on the bubble geometry. Conversely, the injection of gas into liquid metals results in additional problems in measuring the size of the generated bubble, as the medium is not transparent to visible light wavelengths, requiring the use of methods based on X-rays, as in Figure 2.2 (18). Therefore, water models are broadly applied to test ceramic purging plugs (19,20,21). For instance, Gotsis et al. (22) have tested magnesia-spinel porous plugs in a water model, obtaining bubble sizes within a 0.7 to 1.0mm range. However, when the same plugs were evaluated in a 150mm high crucible filled with low-carbon steel, the bubble size was visually estimated between 2 and 5mm on the surface of the molten bath. Thus, the closeness to the industrial

process depends on understanding the influence of each parameter, and whereas some of them have been previously studied (mainly the fluid-dynamic relations) (23), others have been barely investigated. For experimental physical models, it is usual to change the liquid from molten metal to water, maintaining the bubbling gas and the purging device as in the steel ladle. This difference implies that the interfacial energies among these phases are not the same, and the comparison between different media must also consider the influence of the surface wettability on the bubble generation. Thus, bubble generation modelling has attracted a great deal of attention in different fields, such as ore floatation, aluminium foam production and non-metallic inclusion removal in steel ladles. Therefore, a required tool for designing the bubbling process (24,25,26).

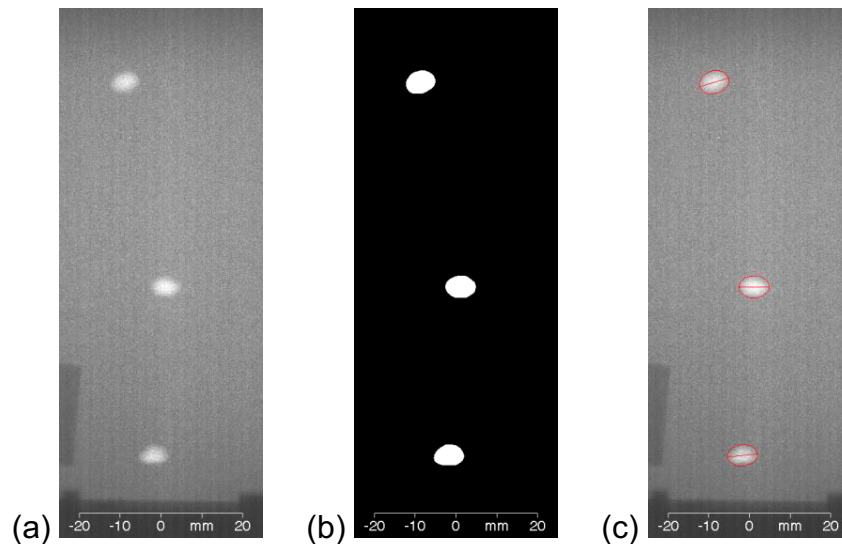


Figure 2.2: Example of bubble size measurement in liquid metal (GaInSn) using X-ray radiography, showing the (a) raw image, (b) the binarised one and (c) the superposition of the detected bubble (18).

The refractory ceramic purging plug has multiple roles in the secondary metallurgy of steels that depend on the applied gas flow rate and the geometry of its capillaries. Although different types of plugs are commercially available, as presented in Figure 2.3, they can be categorised into three kinds of structure. The first one involves the segment, star and slot plugs, comprising straight slits with various geometrical arrangements. These models provide high gas flow rates to be injected into the ladle, aiming at its chemical and thermal homogenization. The second one, the porous plug, is

designed with interconnected open pores, generating small bubbles to capture and remove non-metallic inclusions. The last one, the hybrid plug, combines both structures, aiming at liquid metal homogeneity and cleanliness (14). In summary, using ceramic plugs to remove non-metallic inclusions depends on understanding the generation of bubbles on the porous structure, which prevails for both porous and hybrid plugs.

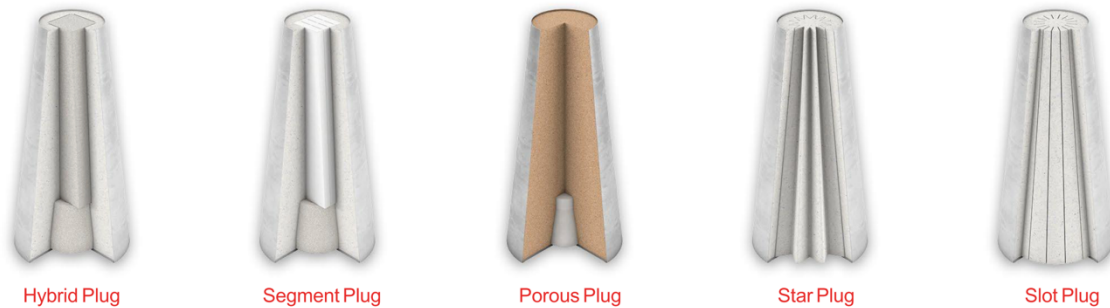


Figure 2.3: Various kinds of commercial purging plugs to inject inert gas into the steel ladle (14).

Microscopically, the plug pores work as individual capillaries, so that the bubble formation on these structures can be divided into three stages: (i) nucleation, (ii) growth, and (iii) detachment of the bubble to the liquid phase, as in Figure 2.4. The nucleation stage is mainly governed by an increase in pressure due to the Laplace pressure effect, attaining a maximum value beyond which the critical growth takes place (27). The detachment stage is almost instantaneous for relatively low gas flow rates and is significant only for the cases where the bubble grows while detaching, for instance, within the transition between the single bubbling and the jetting regimes as the gas flow rate is increased in the purging plugs (28,29,30). It is worth mentioning that, in industrial practice, the removal of non-metallic inclusions in the steel ladle is carried out at relatively low gas flow rates (e. g., ~60 NL/min for a 100-ton ladle (31), where NL/min stands for normal gas litre per minute measured at the temperature of 20 °C and a 1 atm pressure) to reduce the size of the bubble and avoid exposing the liquid steel to the atmosphere. Thus, the stability of the bubble over the purging plug surface is a result of the equilibrium of forces, which depends on its shape during the growth stage and can be directly correlated with the detached bubble volume by assuming an instantaneous detachment (28).

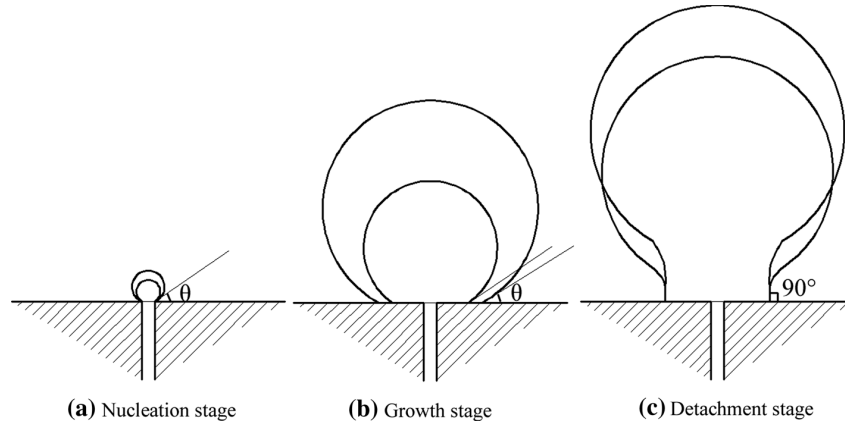


Figure 2.4: Schematic representation of the three stages in bubble formation: (a) nucleation, (b) growth and (c) detachment (28).

Many factors influence the forces involved in the bubble growth step during the gas injection, for instance, gas buoyancy, surface tensions, liquid viscosity, bubble inertia and gas momentum, as represented in Figure 2.5 (28,32). Note that for highly concentrated media, the suspension inertia and the particle-bubble collision can also have a significant effect (30). However, the magnitude of each force component depends on the bubbling regime, which changes from the quasi-static to the dynamic one depending on the gas flow rate through each capillary. Aiming to determine the smallest bubble size that a bubbling device can generate, this work focuses on the quasi-static regime, in which just the buoyancy and surface tension forces are dominant to determine the volume of the detached bubble.

In the quasi-static regime, the buoyancy force (F_b) is calculated by Equation (2.1) as a function of the bubble volume (V_B), the liquid medium density (ρ_l) and the gravitational acceleration (g). Although F_b is sometimes presented in the literature as a function of the density difference between the liquid and the gas ($\Delta\rho = \rho_l - \rho_g$) (30), this approach calculates the difference between the buoyancy and weight of the bubble. As the liquid density is much higher than the gas phase, the weight component can be neglected. Eq. (2.2) describes the force component due to the surface tension (F_σ), which is responsible for sticking the bubble to the plug's orifice and depends on the bubble's base circumference (C_B) and the liquid-gas interfacial tension (σ_{lg}). In principle, one can assume that the growing bubble has a spherical shape (described by the radius of the

bubble's spherical cap - R_B) and that the contact base is restricted to the orifice diameter (D_O) (27). By this simplification, the force components due to buoyancy and surface tension are calculated by Equations (2.3) and (2.4), respectively.

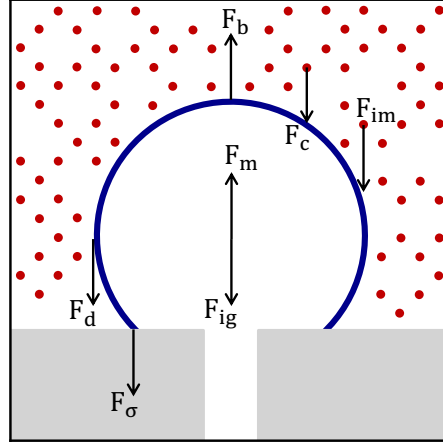


Figure 2.5: Likely forces involved in the generation of bubbles: buoyancy (F_b), surface tension (F_σ), bubble inertia (F_{ig}), liquid drag (F_d), gas momentum (F_m), suspension inertia (F_{im}) and particle-bubble collision (F_c). Adapted from (30).

$$F_b = V_B \rho_l g \quad (2.1)$$

$$F_\sigma = C_B \sigma_{lg} \quad (2.2)$$

$$F_b = \frac{4}{3} \pi R_B^3 \rho_l g \quad (2.3)$$

$$F_\sigma = \pi D_O \sigma_{lg} \quad (2.4)$$

Still considering the quasi-static regime, the bubble detachment takes place when the buoyancy overcomes the surface tension, allowing one to estimate the size of the generated bubble by the equilibrium between F_b and F_σ . This assumption results in Equation (2.5), which has been validated by Sano and Mori (33,34,35) in different liquid media. In their work, silica nozzles were applied to generate bubbles in both wetting (water) and non-wetting (mercury) liquids, and the bubble size in the latter condition was

controlled by the outer diameter of the nozzle (D_{No}) instead of the inner one (D_O). This result suggests the spreading of the bubble base over the nozzle's horizontal surface for non-wetting liquids (high θ), though this effect is limited as the bubble base diameter cannot be larger than D_{No} . Consequently, a marginal increase in the detached bubble diameter may be observed depending on the contact angle between the nozzle and the liquid.

$$D_B \cong \sqrt[3]{\frac{6 \sigma_{lg} D_O}{\rho_l g}} \quad (2.5)$$

The ceramic plug structure is better described as a perforated plate instead of individual nozzles because no outer diameter is associated with each pore. Thus, Equation (2.5) is not suitable to model the influence of the plug's chemical composition over bubbling, as the bubble base is allowed to spread over the plug surface rather than being restricted by an outer nozzle diameter, as shown in Figure 2.6. In fact, experimental results from the literature highlighted that lowering the surface wettability by chemical modification leads to a change in the bubble shape and an increase in the detached volume (36,37). Lin et al. (37) assessed the influence of the surface wettability on the generation of air bubbles in a water model using a stainless-steel drilled plate (orifices of 0.25 and 0.50mm), which was treated by plasma polymerisation to modify the solid surface energy, setting different contact angles in the range of 5.0 to 99.7°. Their results pointed out that the orifice diameter is dominant over the contact angle to determine the volume of the detached bubble on hydrophilic surfaces ($\theta < 55^\circ$). On the other hand, the bubble's base in contact with the plug spreads over the surface for higher contact angles, which causes the detached volume to increase, converging to an equal final value regardless of the orifice diameter. Therefore, the experimental results suggest a major role of the pore diameter for low contact angles, which becomes negligible as the surface wettability is decreased.

In summary, applying Equation (2.5) to ceramic plugs underestimates the bubble size for non-wetting surface compositions, commonly used to prevent the liquid steel infiltration (38). Consequently, the plug would generate larger bubbles than predicted, displacing their size distribution out of the optimum range for inclusion capturing and

removal. Additionally, to the best of our knowledge, the bubbling models presented in the literature have not been applied to steel ladle ceramic plugs. Therefore, this work aims to study the current models for bubble generation, considering the influence of both the pore geometry and the composition. The calculated values from the simulations are compared to the experimental results by Lin et al. (37) so that their convergence can validate the model.

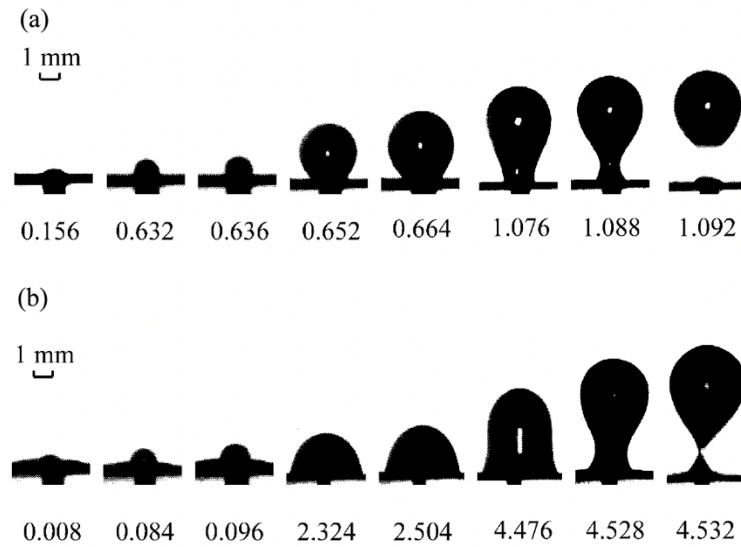


Figure 2.6: Bubble formation in (a) wetted and (b) poorly wetted surfaces - a contact angle (θ) of 68 and 110°, respectively. Time in seconds (36).

2.3 Methodology

Terashima et al. (39) considered the influence of the surface wettability by assuming that a spherical bubble grows over the bubbler surface while keeping the contact angle (θ) at the equilibrium value, as represented in Figure 2.7a. According to Young's equation, the θ angle is defined by the equilibrium among the interfacial tension solid-gas (σ_{sg}), solid-liquid (σ_{sl}) and liquid-gas (σ_{lg}), as expressed in Equation (2.6).

$$\sigma_{sg} - \sigma_{sl} = \sigma_{lg} \cos \theta \quad (2.6)$$

The volume of the growing bubble (V_B) is derived by Equation (2.7) considering the spherical cap of gas over the bubbling surface, as delimited by the solid blue line in

Figure 2.7a. Then, applying Equation (2.7) to Equation (2.1) results in the buoyancy force (F_b) expressed by Equation (2.8) (39,32,28).

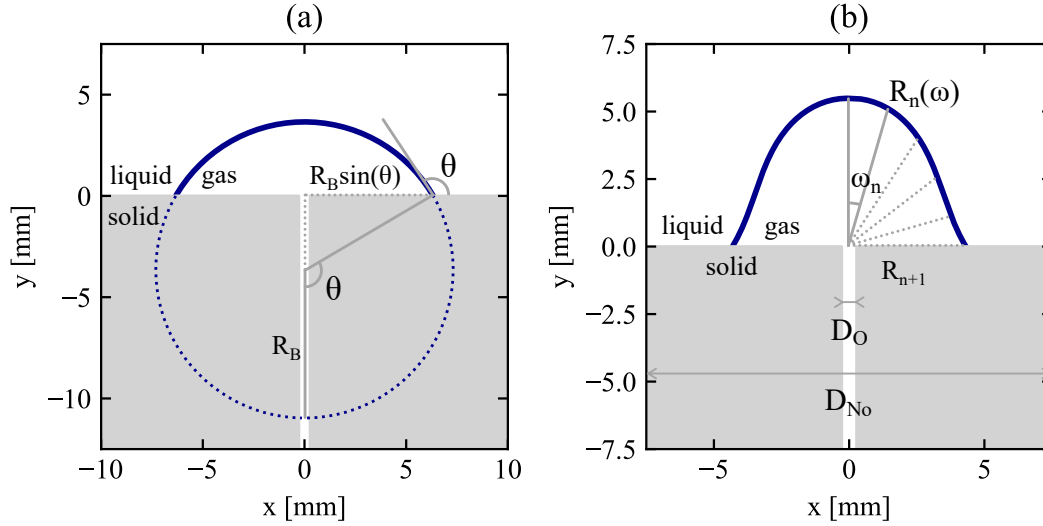


Figure 2.7: Schematic bubble profile based on a contact angle of 120° , considering (a) a spherical-shaped approximation and (b) the energy-minimised shape.

$$V_B = \frac{\pi}{3} R_B^3 (2 - 3 \cos \theta + \cos^3 \theta) \quad (2.7)$$

$$F_b = \frac{\pi}{3} R_B^3 (2 - 3 \cos \theta + \cos^3 \theta) \rho_l g \quad (2.8)$$

As the bubble spreads over the horizontal surface of the bubbler, the perimeter of its circumference base (C_B) is calculated by projecting R_B on the horizontal plane, as stated by Eq. (2.9). Although it would be straightforward to calculate the force due to the interfacial tension based on Equation (2.2), the literature often considers the projection of the interfacial tension (σ_{lg}) on the vertical axis by $\sin\theta$, resulting in Equation (2.10) to calculate F_σ (39,32,28). The implications are further discussed in the results.

$$C_B = 2 \pi R_B \sin \theta \quad (2.9)$$

$$F_\sigma = 2 \pi R_B \sigma_{lg} \sin^2 \theta \quad (2.10)$$

The bubble will detach when F_b overcomes F_σ , as these forces act in opposite directions. Therefore, Equation (2.11) is derived based on Equations (2.8) and (2.10), and it defines the diameter of the equivalent bubble (D_B) at the end of the growth stage as a function of the surface wettability (θ). Equation (2.11) shows that D_B would tend to zero when the contact angle decreases, as the orifice diameter is not considered in this model because the bubble is allowed to spread over the bubbler surface. Thus, D_o would become determinant to dictate the bubble size when the contact angle tends to zero, so that Equation (2.5) can be applied to estimate D_B (39). Moreover, D_B is analytically obtained by Equation (2.11) as the gas volume (V_B) and the contact base (C_B) can be expressed as a function of R_B for spherical-shaped bubbles (Equations (2.7) and (2.9), respectively).

$$D_B \cong 2 \sqrt{\frac{6 \sigma_{lg}}{\rho_l g}} \sqrt{\frac{\sin^2 \theta}{[2 + 3 \cos \theta - \cos^3 \theta]}} \quad (2.11)$$

When the bubble diverges from a spherical shape in the quasi-static regime, or even when considering the complexity of the dynamic regime of bubbling (32,28), its diameter cannot be obtained by an analytical solution. This shows the need to implement a numerical method to calculate the size of the detached bubble by trial and error. As a matter of illustration, if a numerical method is applied to solve Equations (2.8) and (2.10), a set of different R_B values would be iteratively tested up to F_b equals F_σ .

Thus, Sonoyama and Iguchi (40) developed a model to obtain the geometry of the growing bubble by calculating the minimum energy state associated with its shape. The routine initiates with the discretisation of the bubble profile in “n” elements given in polar coordinates by the linear and angular terms, R_n and ω_n , respectively, represented in Figure 2.7b and discretised as in Equation (2.12). The bubble’s energy (E_B) is calculated by Equation (2.13), which comprises three terms: (i) the gravitational potential energy, taken as negative as the bubble is formed on the upper surface (see Figure 2.7b), (ii) the liquid-gas interfacial energy (γ_{lg}) and (iii) a change from the solid-liquid (γ_{sl}) to the solid-gas (γ_{sg}) interface as the bubble spreads over the bubbler surface. It is important to notice that the contact angle term (θ) in Equation (2.13) represents the equilibrium among the surface tensions, as for Young’s equation (Equation (2.6)). Thus, this model differs from other

approaches in the literature, which restrict the bubble base geometry to a constant contact angle (or even within a range) to take the effect of the surface wettability on bubbling into account (41,42,43).

$$\begin{cases} \bar{\omega} = (\omega_1, \omega_2, \omega_3, \dots, \omega_{n+1},) \\ \bar{R} = (R_1, R_2, R_3, \dots, R_{n+1},) \end{cases} \quad (2.12)$$

$$\begin{aligned} E_B = & \underbrace{-\frac{\pi}{2}(\rho_l - \rho_g) g \int_0^{\pi/2} R(\omega)^4 \cos \omega \sin \omega d\omega}_{(i)} + \\ & \underbrace{+ 2\pi \gamma_{lg} \int_0^{\pi/2} R(\omega) \sqrt{R(\omega)^2 + \left(\frac{\partial R}{\partial \omega}\right)^2} \sin \omega d\omega}_{(ii)} + \\ & \underbrace{+ \pi \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg} \cos \theta} (R_{n+1}^2 - D_0^2/4)}_{(iii)} \end{aligned} \quad (2.13)$$

An iterative routine allows one to minimise the bubble's energy to obtain its stable shape. The routine begins with an initial condition representing a starting bubble profile, which is calculated as a hemisphere of volume V_B by Equation (2.14). Then, E_B from Equation (2.13) is minimised by changing the linear coordinates of each element (R_n) via an iterative routine, so that the shape of the growing bubble with volume V_B is obtained. Therefore, a crucial constraint throughout the routine is to keep the bubble volume at each iteration ($V_{B,i}$) close to the set value (V_B), as represented in Equation (2.15). Additionally, to simulate the influence of the bubbler geometry, the inequality of Equation (2.16) must also be obeyed, which defines that the linear coordinate of the bubble contact base (R_{n+1}) must be greater or equal to the inner diameter of the orifice (D_0) and less or equal to the outer diameter of the nozzle (D_{N0}), as in Figure 2.7b.

$$R_n = \sqrt[3]{\frac{3 V_B}{2\pi}} \quad (2.14)$$

$$V_{B,i} = \frac{2}{3} \pi \int_0^{\pi/2} R(\omega)^3 \sin \omega d\omega \approx V_B \quad (2.15)$$

$$D_0 \leq 2 R_{n+1} \leq D_{No} \quad (2.16)$$

The forces due to buoyancy and surface tension are now calculated considering the bubble shape obtained by the energy minimisation method, which may or may not deviate from the spherical one. A contact base length (C_B) is obtained for each bubble volume (V_B), allowing one to determine whether the growing bubble is stable at the bubbler surface by comparing the force components of Equations (2.17) and (2.18). Thus, the volume of the detached bubble is obtained when $F_b > F_\sigma$ and can be hypothetically expressed by its equivalent diameter (D_B), calculated using Equation (2.19) by assuming that the bubble will tend to a spherical shape while rising in the liquid medium. This assumption is valid for D_B values below 1mm (44).

$$F_b = \frac{2}{3} \pi \int_0^{\pi/2} R(\omega)^3 \sin \omega \, d\omega \, \rho_l g \quad (2.17)$$

$$F_\sigma = 2 \pi R_{n+1} \sigma_{lg} \quad (2.18)$$

$$D_B = \sqrt[3]{6 V_B / \pi} \quad (2.19)$$

The calculations were carried out using scripts in *Python 3.8* from the Anaconda distribution (45) with the following packages: *Matplotlib (3.4)* for the plots, *Numpy (1.20)* for the numerical calculations and *Scipy (1.7)* for the optimisation algorithm. The obtained results related to the influence of the surface wettability (θ) on the detached bubble volume were validated by using the experimental results by Lin et al. (37). As their experimental setup comprised the injection of compressed air into a water model, the properties presented in Table 2.1 were considered for the calculations in this work.

Table 2.1: Properties of the water model bubbled with compressed air.

Property	γ_{lg}	ρ_l	ρ_g
Value	72.8 $\mu\text{J m}^{-2}$	1000 kg m^{-3}	1.2 kg m^{-3} (20°C;1atm)
Reference	(46)	(23)	(47)

2.4 Results and discussion

2.4.1 The spherical-shaped bubble model

Based on the properties of Table 2.1, Equation (2.11) estimates the bubble diameter generated by a capillary as a function of the surface wettability (θ). The results are compared to the experimental data by Lin et al. (37) using the same contact angles as in their work. Figure 2.8 presents the convergence analysis between the experimentally obtained bubble diameters and the calculated values for two different orifice diameters. In these figures, relative errors for the D_B range from -73 to +79% for contact angles below 45° , whereas the maximum deviation (+122%) is obtained for the 0.25mm pore with $\theta = 45.7^\circ$. The model proposed by Terashima et al. (39) relies upon decomposing the liquid-gas interfacial tension in the vertical direction by $\sin\theta$ as discussed for Equation (2.10), which is still under debate in the literature (28,30,27). In practice, the error values for the bubble diameter could be even higher if the σ_{lg} decomposition was avoided, mainly for angles different from 0 and 90° , where $\sin\theta > \sin^2\theta$ leads to the increase of D_B in Equation (2.11). In fact, the force component related to the interfacial tension would increase, keeping the bubble attached to the surface and resulting in a volume increase. Moreover, it is reasonable not to decompose the interfacial energy, as the contact angle of the bubble base will tend to 90° due to the necking prior to the detachment stage (28).

The negative error for the lowest contact angle (5°) is already expected, as the orifice diameter (D_O) is not considered in the model by Terashima et al. (39) - Equation (2.11). In contrast, the experimental results by Lin et al. (37) show larger bubble diameters as their base cannot be smaller than D_O . This restriction increases the F_σ component - Equation (2.10) - and, consequently, enhances the interfacial adherence between the bubble and the solid material. Note that for contact angles above 70° , the error values always become positive and range within 77 to 88%. Large positive errors for high θ values are mainly associated with the shape of the bubble, which is assumed to be spherical throughout the whole range of contact angles. In fact, the literature shows a divergence from this approach, as the experimental results by Gnyloskurenko *et al.* (48) show that the bubble shape deviates from the spherical one as the surface wettability decreases (high contact angles).

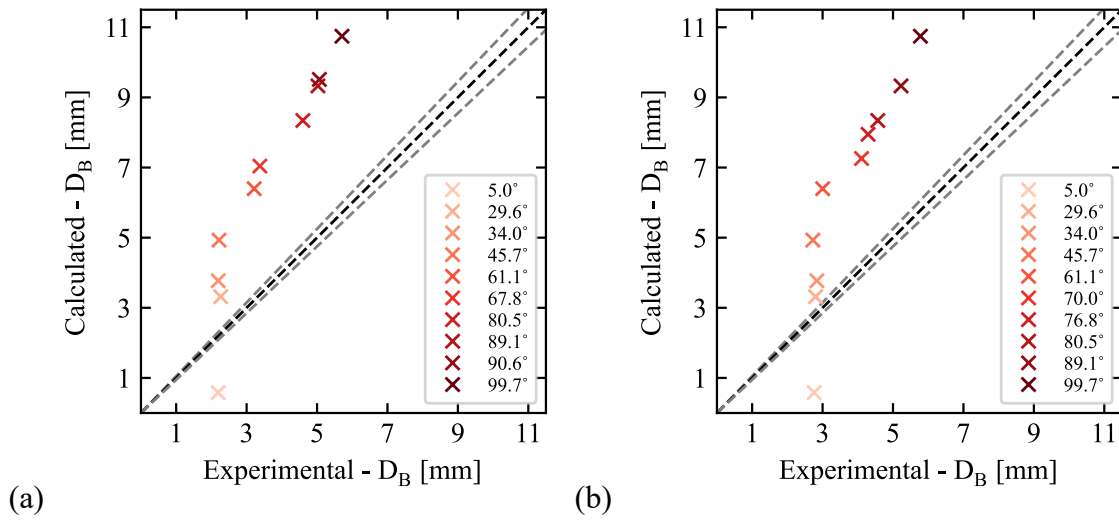


Figure 2.8: Convergence analysis between the experimental data by Lin et al. (37) and the calculated values of bubble diameter (Equation (2.11)) for orifice sizes of (a) 0.25mm and (b) 0.55mm. The dashed grey lines represent an error of $\pm 5\%$.

2.4.2 The shape-corrected bubble model

The model proposed by Sonoyama and Iguchi (40) - Equations (2.12) to (2.16) - considers the effect of surface wettability to predict the bubble shape based on the minimisation of its energy. Figure 2.9 shows the bubble profile as a function of the contact angle for a given D_O in the water-air system. The result highlights the change of the bubble shape due to the surface wettability, pointing out the divergence from the spherical shape mainly for contact angles above 30° , which induces a change in the detached bubble volume. Thus, still considering the detachment criterion ($F_b > F_\sigma$), a more accurate model can be proposed to predict the influence of θ on the size of the generated bubble based on its corrected shape.

The evaluation of the forces due to buoyancy (F_b) and surface tension (F_σ) can be used to predict whether a given volume of gas will be enough to result in bubble detachment. As the criterion ($F_b > F_\sigma$) is satisfied, the equivalent bubble diameter is obtained via Equation (2.19). Accordingly, a set of bubble volumes must be tested to determine the diameter of the detached bubble for each contact angle. Applying this routine to the water-air system (Table 2.1), the obtained results are compared to experimental ones in a-b. The bubble diameters obtained by the model of energy minimisation show a strong correlation with the experimental data. For contact angles

below 30° , the error is positive and restricted to 10% for both orifice diameters (Figure 2.10c-d). For θ values above 70° , the errors are limited to a maximum of 6% ($D_O = 0.55\text{mm}$ and $\theta = 76.8^\circ$), highlighting the correlation between the experimental and the calculated data. The highest errors are obtained for intermediate values of θ , in the transition zone from the pore-dominated region to the material-dominated one.

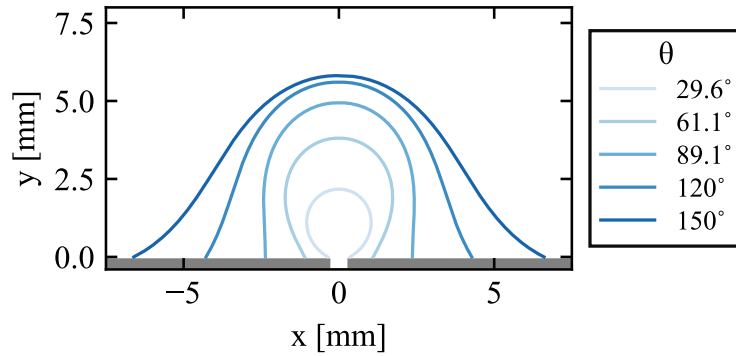


Figure 2.9: Influence of the surface wettability (θ) on the shape of the largest bubble volume still stable on the bubbler surface, for an orifice diameter of 0.55mm (49).

Up to this point, the contact angle has been discussed based on the force equilibrium among the interfacial energies, as defined by Young's equation (Equation (2.6)). However, this thermodynamic equilibrium is observed only for ideal surfaces, defined as smooth, chemically homogeneous, rigid and non-reactive ones (50). Methods for measuring contact angles typically experience the static (θ_s), the advancing (θ_{adv}) and the receding (θ_{rec}) angles, and the difference between θ_{adv} and θ_{rec} is named as the contact angle hysteresis. It is worth noting that the terms “advancing” and “receding” come from the experimental measurement where the liquid is injected and withdrawn. For the sake of bubbling, the opposite situation takes place, as the liquid recedes while the gas expands over the solid surface, and vice versa. For instance, Mirsandi et al. (42) measured θ_s , θ_{adv} and θ_{rec} for a set of solutions with different surface tensions (σ_{sg}), obtaining static contact angles roughly in the range between 80° and 110° . Throughout their measurements, the static value was close to the receding one for low contact angles, whereas it approached the advancing angle for high contact angles, even though the θ hysteresis was constant and close to 10° (related to the surface roughness, equal to $0.211\mu\text{m}$ on average).

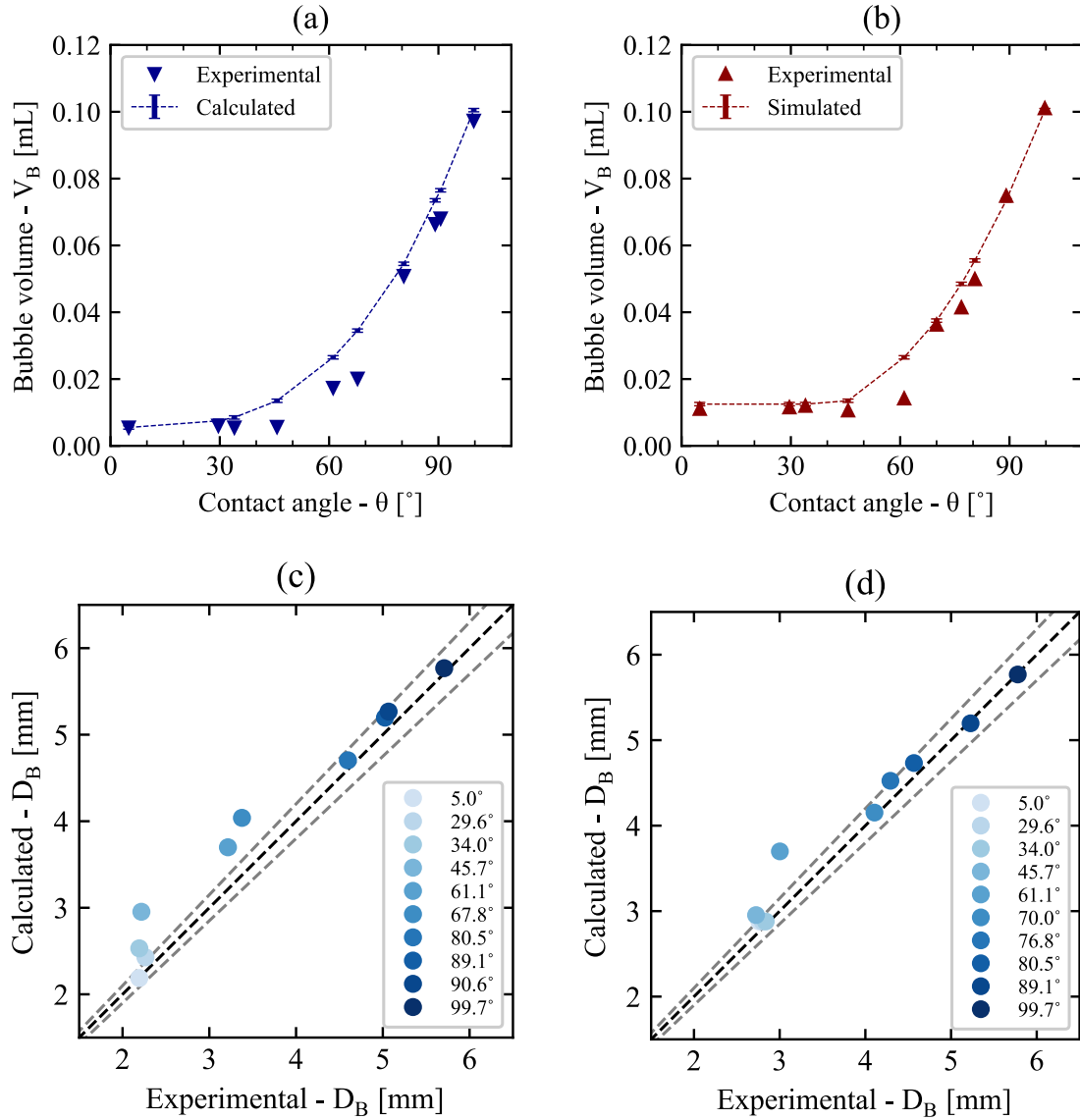


Figure 2.10: Analysis of convergence between the experimental data (37) and the calculated values of bubble volume (Equations (2.12)-(2.19)) and diameter for orifice sizes of (a, c) 0.25mm and (b, d) 0.55mm. The dashed grey lines represent an error of $\pm 5\%$.

This discussion can be expanded to understand the larger errors obtained in Figure 2.10 for intermediate contact angles (30 - 70°), as the experimental data reported by Lin et al. (37) was measured under an equilibrium condition (15 seconds after the drop of the liquid over the solid surface) and represents the static contact angle. Thus, as the growth of the bubble base is associated with the receding of the liquid, the measurement of θ_{rec} would better represent the condition prior to bubble detachment. Additionally, although

the quasi-static regime assumes no influence of the gas flow rate on the generated bubble, the bubble base is in a constant process of expansion and shrinkage over the solid surface, so that the contact angle is not under an equilibrium condition. This phenomenon becomes evident in the experiments carried out by Lin et al. (37), where the increase in the gas flow rate within the quasi-static regime resulted in a decrease in the gas volume on hydrophobic surfaces, which is associated with a non-equilibrium condition of bubbling. Besides that, this effect is not observed for very low contact angles, as the bubble base is restricted to the orifice diameter and does not expand over the solid surface.

2.4.3 The combined model

Despite the very good correlation between the experimental data and the shape-corrected model, the application of this routine still shows a high computational time consumption when compared to simpler models, e.g., the ones presented in Equations (2.5) and (2.11). Even so, the experimental volume of the detached bubble volume converges to the same value for high contact angle surfaces, regardless of the orifice diameter (37). The same situation is obtained from the calculations based on the shape-corrected model, as in Figure 2.10a-b. Additionally, when the material has a small influence on the bubbling (low θ), the bubble's contact base is restricted to the orifice diameter, and its shape is close to a sphere. Thus, combining the current models could lead to a time-saving solution for estimating the bubble size generated in perforated plates.

On the one hand, Equation (2.5) seems to be an accurate estimate of the equivalent diameter of the detached bubble for low contact angles, with errors below $\pm 2\%$ for 0.25mm pores with $\theta \leq 45.7^\circ$ and below $\pm 6\%$ for 0.55mm pores with $\theta \leq 61.1^\circ$. On the other hand, the material-dominated region of bubbling would be predicted by the shape-corrected model with an orifice diameter tending to zero, in other words, considering only the material's effect. The result for the combined model is presented in Figure 2.11, where the pore-dominated region (I in Figure 2.11) is predicted by Mori's model (35) (dashed lines obtained from Equation (2.5)) whereas the material-dominated region (III in Figure 2.11) is represented by the calculations of the shape-corrected model, assuming a null pore diameter. The latter model is represented by the solid line in Figure 2.11 and corresponds to setting D_o equal to zero in Equations (2.13) and (2.16) so that the orifice

influence is neglected throughout the calculations. The intersection point of the two curves can be associated with the transition (II in Figure 2.11) between these two regions. When the contact angle approaches 145° , the uncertainty to estimate D_B increases. The model is not able to predict the bubble geometry for angles beyond this value (IV in Figure 2.11). The reason is that surfaces with $\theta > 150^\circ$, the so-called “superhydrophobicity”, show very low wettability of the liquid phase. The gas phase tends to spread over the solid surface, forming a thin film at the initial stages of bubble formation (51). These superhydrophobic surfaces are not of practical interest for bubble generation as they result in bubble coalescence in multiple hole systems, drastically increasing D_B .

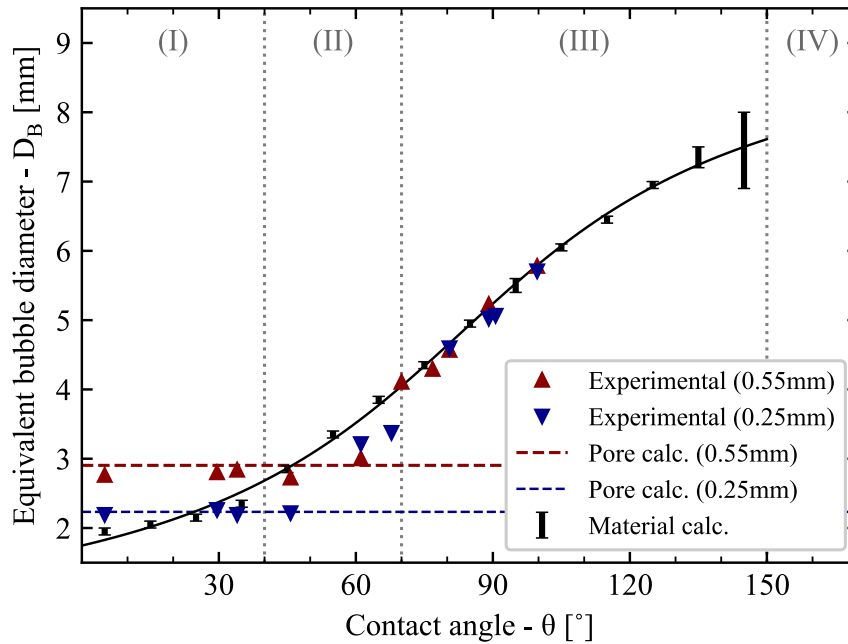


Figure 2.11: Equivalent bubble diameter (D_B) as a function of the surface contact angle (θ) obtained by the combined model compared to the experimental data (37), defining the following regions: (I) pore-dominated, (II) transition, (III) material-dominated and (IV) superhydrophobic.

The combined model could be further applied as a tool to estimate the bubble size behaviour for other bubbling systems. To illustrate it, the injection of argon into metallurgical ladles aiming to withdraw SiO_2 inclusions from steel can be studied ($\gamma_{lg} = 1.82\text{J/m}^2$ and $\rho_l = 7020\text{kg/m}^3$ (52)). For this matter, the contact angle (θ) among the phases

is determined by the ceramic plug material, as the steel composition is dictated by the process, and the injected inert gas is restricted to argon. In Figure 2.12, the dashed lines represent the pore-determined D_B value for 100 and 250 μm -pores (Equation (2.5)), whereas the solid line represents the material-determined D_B value considering oxide and non-oxide ceramics (Equations (2.13)-(2.19)). For the steel-argon system, the ceramic plug material plays a major role for $D_O \leq 250\mu\text{m}$ so that no pore-dominated region is expected. Although the current commercial plugs based on Al_2O_3 and MgO show a good performance regarding the resistance to infiltration (38), these compositions result in the largest bubble diameters. For instance, the ideal D_B value to withdraw silica inclusions from liquid steel ranges within 1 and 5 mm based on kinetic aspects, which is restricted within the 1.5 - 2mm range when the thermodynamic aspects are coupled (17,26). In this case, according to the calculations, the silicon carbide compositions could generate the smallest bubble sizes in liquid steel. Additionally, one must be aware of the gas expansion along the bubble's ascension in the steel ladle due to the ferrostatic pressure drop and the thermal equilibrium with the liquid metal (53). Thus, the surface wettability establishes a trade-off between the resistance to infiltration of liquid metal in the purging plug and the generation of small bubbles capable of removing inclusions, as these targets are better addressed with high and low contact angles, respectively. However, it is worth noting that the wettability acts at different moments for each effect because the bubble spreads over the horizontal surface of the ceramic plug during bubbling, whereas the infiltration is controlled by the capillary wall underneath the pore (38). Coupled with cutting-edge manufacturing techniques (i.e., additive manufacturing), these fundamentals could be further applied to develop infiltration-delayed ceramic plugs, also able to generate small bubbles.

The application of the combined model is not restricted to predicting the bubble size, as the obtained results also provide a comparison of bubbling under different conditions. As discussed, water models are typically designed to simulate the behaviour of ceramic plugs in steel ladles based on their fluid-dynamic relations. However, the contact between the solid surface and the liquid medium must also be considered to study ceramic plugs regarding bubble generation. For instance, a MgO plug presents a contact angle of 130° with the liquid steel, whereas the same composition displays a θ value of 44.5° in contact with water (54,55), so that the surface wettability is an additional

parameter to be considered when designing a water model to test the performance of ceramic plugs. Therefore, by predicting both the influence of the pore and the material on the bubbling behaviour of a capillary structure, the development of a combined model opens up an avenue to overcome challenges in various industrial practices that deal with the injection of bubbles in liquid columns.

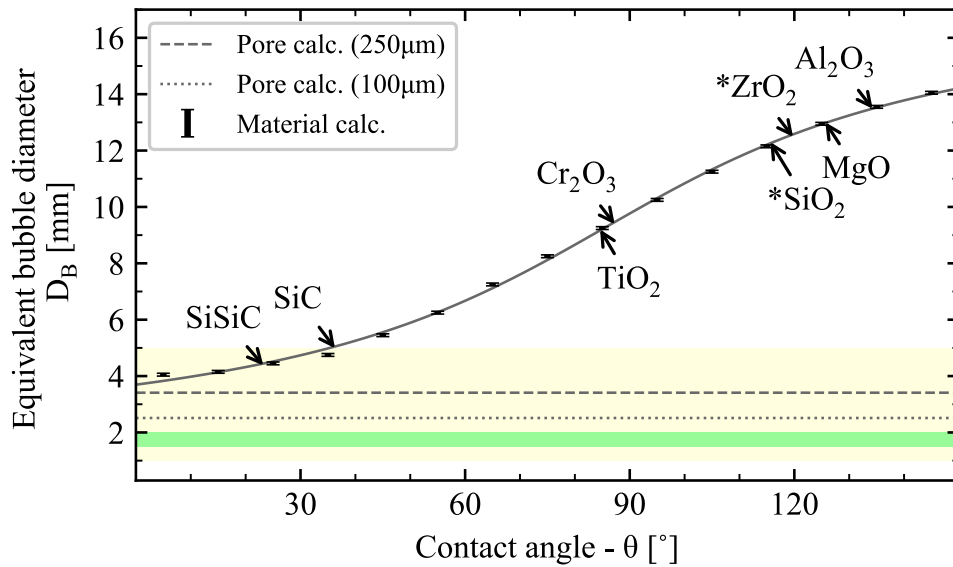


Figure 2.12: Equivalent bubble diameter (D_B) as a function of the surface contact angle (θ) calculated for the injection of argon gas in liquid steel and compared to ceramic compositions at 1550°C (*) and 1600°C (56,57). The ideal and optimum ranges of D_B are also shown in yellow and green, respectively.

2.5 Conclusion

This work studied the injection of gas bubbles in liquid media through capillary structures, analysing the comparison between the experimental data from a water-air system and the available models in the literature. A first approach to consider the influence of the surface wettability on the size of the generated bubble assumes that the growing volume of gas maintains a spherical shape over the bubbler surface, according to its contact angle. This model predicted that the bubble diameter scales with the contact angle, although the obtained values were highly overestimated when compared to the experimental data. For $\theta > 70^\circ$, the relative errors ranged within 77 and 88% because,

experimentally, the shape of the growing bubble diverges from the spherical one as the surface wettability is lowered, violating the model's assumption.

A shape-corrected model was developed by adjusting the shape of the growing bubble over the ceramic solid surface based on an energy minimisation routine and the detachment criteria ($F_b > F_\sigma$). When compared to the experimental data, the relative errors were upper limited by 6% for contact angles above 70° , presenting a very good correlation to predict the effect of the material on the generated bubble. However, the shape-corrected model on its own showed a high computational time consumption, requiring its combination with a well-established model in the literature (which takes just the influence of the pore diameter into account).

The combined model seemed to be a time-saving solution to predict the influence of both the bubbler geometry and composition (surface wettability). Based on the results, four bubbling regions were defined: (i) the pore-dominated one, well established in the literature's models; (ii) the transition region, in which the bubble detaches in a non-equilibrium condition (iii) the material-dominated one, influenced by the contact angle among the phases; and (iv) the superhydrophobic region, in which the bubble tends to be a thin gas film over the surface. Thus, the application of the combined model broadened the possibilities to study systems other than the water-air one.

To illustrate this, the injection of bubbles in steel ladles aiming at removing non-metallic inclusions was analysed, and the results pointed out the importance of wetting surfaces (low contact angles) to generate bubbles within the ideal range of size to produce clean steels. On the other hand, ceramic refractories in contact with molten steel typically exhibit a high contact angle to avoid the infiltration of liquid into their pores. Therefore, the trade-off between bubbling ideal diameters and avoiding liquid steel infiltration highlights the importance of surface wettability when designing a ceramic plug to produce a clean steel. Furthermore, the combined model for bubbling can be applied as an additional criterion to design physical simulators for the metallurgical ladle.

CHAPTER 3 – WETTABILITY OF NON-METALLIC INCLUSIONS AND ITS IMPACT ON BUBBLE-INDUCED FLOTATION KINETICS

3.1 Introduction

In the wake of bubble-induced flotation, this chapter introduces the design of physical models to understand the kinetics of particle removal. Several factors must be considered when extrapolating the behaviour of high-temperature reactors from steelmaking to room-temperature water models. For instance, when selecting a particle to reproduce non-metallic inclusions, variables to be addressed include size distribution, geometry, wettability and relative density compared to the liquid medium. Therefore, this chapter explains how the experimental procedure was developed to ensure accurate measurement of particle concentration over time, enabling flotation experiments to be carried out. To illustrate, two types of buoyant particles - one hydrophilic and the other hydrophobic - are presented in the results, demonstrating that bubble injection can slow the removal of buoyant hydrophilic particles and, conversely, enhance the removal efficiency of hydrophobic ones.

3.2 Literature review

Various sources of non-metallic inclusions might be pointed out throughout the refining of liquid metal, as seen in Figure 3.1. Whereas some can be lessened by properly installing flow control devices and adjusting the slag and mould powder's chemical composition (58,59), others are inherent to steelmaking – namely, the contact with ceramic refractories and the deoxidation of liquid metal (generating oxide inclusions), making the removal of non-metallic inclusions a recurrent challenge for metallurgists. Although these ceramic phases are typically less dense than the molten bath, their natural flotation velocity is governed by Stokes' Law, according to which μm -sized inclusions would take hours (or even days) to reach the slag layer of a steelmaking ladle (60). Consequently, injecting inert gas bubbles is crucial to the induced flotation of inclusions, speeding up the refining of the liquid metal.

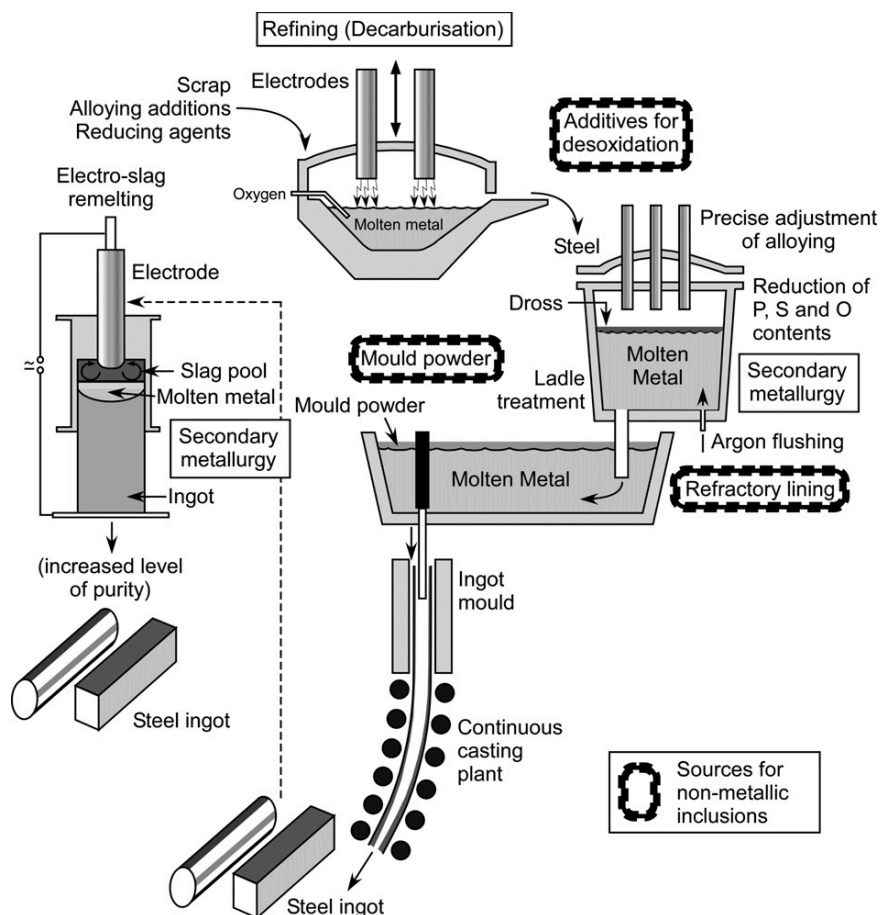


Figure 3.1: Schematic diagram of steel refining, highlighting the sources of inclusions (61).

Removing non-metallic inclusions (NMI) is one of the targets for the secondary refining of steels. It is conducted by injecting inert gases through porous bubblers either in the ladle or in the tundish. From a macroscopic point of view, the bubble plume interacts with the molten metal to capture inclusions, carrying them to the slag layer (26,62). If properly adjusted (i.e., in chemical and rheological aspects), this top molten layer irreversibly dissolves the NMI, enhancing the cleanliness of the molten bath (63). On the other hand, understanding the underlying microscopical mechanisms allows one to tune the process parameters and increase the removal rate and efficiency of the bubble-induced flotation, which might also lead to the development of porous bubblers, also known as purging plugs (64). On top of natural flotation, bubbling in the liquid metal provides additional mechanisms of induced flotation by which inclusions may be removed, as represented in Figure 3.2: (A) attachment to the bubble surface, according to the probabilities of collision, adhesion and detachment (26); (B) captured in the bubble's

wake zone, after entering the rising zone (8,15); (C) carried by the flow pattern caused by the bubble plume (65). It is worth noting that only mechanism “A” relies on a three-phase contact among the inclusion, the gas bubble, and the liquid medium. Thus, it may become relevant to investigate the interface tensions and their influence on the attachment step (66). Additionally, the injection of bubbles causes the agglomeration of fine inclusions into coarser ones, speeding up their removal (67).

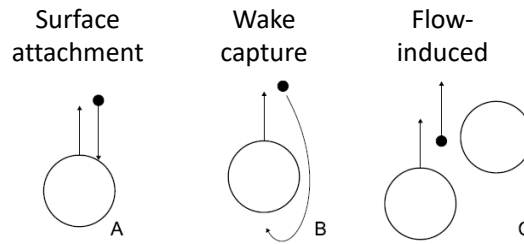


Figure 3.2: Mechanisms involved in the bubble-induced flotation of particles in liquid media (8,15).

The thermodynamics of particle attachment has been previously investigated [8] and could be summarised as depicted in Figure 3.3. From the moment when the bubble-particle collision takes place, the three-phase contact line defines an angle for the particle on the bubble’s surface (θ). By increasing this angle, the particle moves towards the bubble, facing an energy barrier to its attachment (ΔE_a). Thus, the magnitude of this energy barrier can be related to the ease with which inclusions can be captured. Once overcome, the system seeks a local minimum energy point corresponding to the stable contact angle (θ_e). In some cases, typically for liquidphobic inclusions (green line), this point also corresponds to a global minimum, so the inclusion is unlikely to detach back into the liquid phase. For it to occur, the particle would need enough energy to overcome a detachment barrier (ΔE_d), which is higher than the attachment one (ΔE_a) when the latter represents a lowering in the system energy (i.e., $\Delta E_{att} < 0$). Conversely, for liquidphilic particles, the detachment barrier may be either lower than the attachment one (orange line, where $\Delta E_{att} > 0$) or even non-existent (red line). In the former case, the particle could still be attached to the bubble surface, though in a metastable state, as it does not correspond to a global minimum energy point (68).

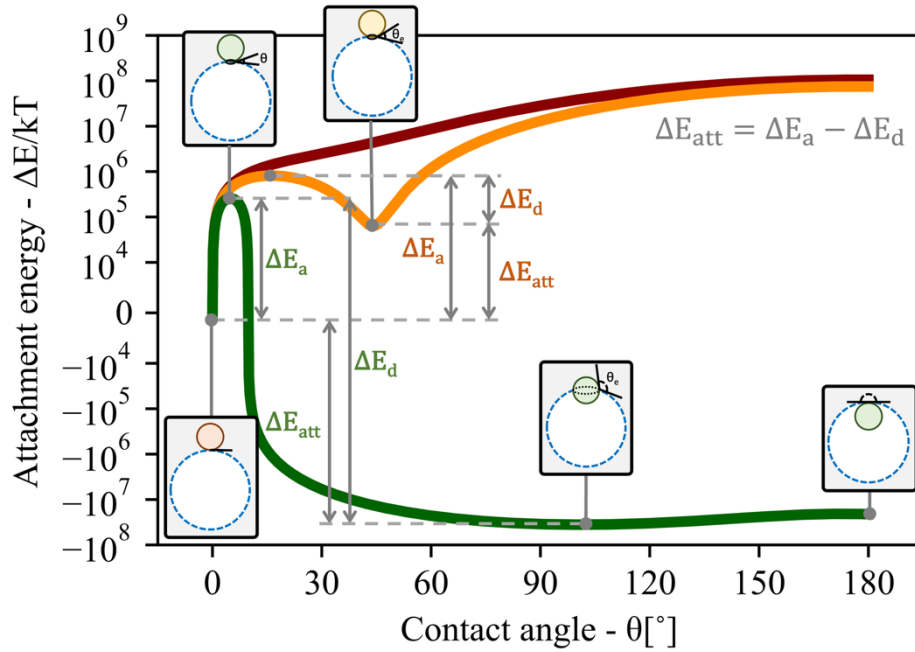


Figure 3.3: Typical energy curve for the attachment of particles with low (red), intermediate (orange) and high (green) contact angles. Adapted from (17).

Another aspect is the design of the experiment in water models, which includes variables such as the vessel's geometry, the liquid medium, the gas bubbler and solid particles. Starting from the model's geometry, it is usual to rescale industrial facilities while keeping the proportions within their features. For that, the literature presents examples for the steel ladle (69), tundish (70), ladle shroud (71) and continuous casting mould (72). On the other hand, some works try not to reproduce a specific reactor, but to isolate variables affecting the particle removal, such as turbulence by an impeller (73), the optimum distance between orifices in the bubbler (74), or the contribution of the bubble wake in the overall removal of particles (as inclusions) (15).

When rescaling a specific geometry, it is crucial to base it on similarity criteria, such as those from dimensionless numbers in fluid dynamics. The Reynolds number (Re) is described by Equation (3.1) as a function of the velocity (V), the length (L), the liquid density (ρ_l) and viscosity (μ_l). A comparable Re value between the model and industrial vessels ensures equivalent turbulence, as the ratio of inertial to viscous forces is maintained. Thus, naming λ as the scale factor between the water model (subscript "M") and the industrial prototype (subscript "P"), and considering that water and liquid steel have similar kinematic viscosity ($\eta = \mu/\rho$), Equation (3.2) is obtained. It represents how

velocities should be scaled in the model to keep the same Re. Also, the Froude number (Fr) is introduced in Equation (3.3), considering the gravitational acceleration (g) and the variables above. It establishes the ratio of inertial to gravitational forces so that bulk flow phenomena are well reproduced in the water model, and applying the same procedure, Equation (3.4) is obtained. Analysing Equations (3.2) and (3.4) together, one might notice that both criteria are met only when the scale factor equals the unit ($\lambda = 1$) (70). Thus, any rescaling involves a trade-off when designing water model simulations, not to mention additional similarity criteria related to bubbles and particles.

$$\mathbf{Re} = \frac{\mathbf{V L \rho}}{\mu} \quad (3.1)$$

$$\mathbf{V_M} = \frac{1}{\lambda} \mathbf{V_P} \quad (3.2)$$

$$\mathbf{Fr} = \frac{\mathbf{V^2}}{\mathbf{g L}} \quad (3.3)$$

$$\mathbf{V_M} = \sqrt{\lambda} \mathbf{V_P} \quad (3.4)$$

Also, the particle selection across the available grades should consider the behaviour of non-metallic inclusions in molten metal. A similarity criterion has been discussed in the literature based on the particle's terminal velocity (V_r), as defined by Stokes' law - Equation (3.5), as a function of the particle diameter (D_p), the densities of liquid (ρ_l) and particle (ρ_p) and viscosity of liquid (μ_l) (70). To scale the terminal velocity proportionally and assure the similarity of inclusion trajectory while keeping the Fr constant, i.e. obeying Equation (3.4), the particle size ($D_{p,M}$) and density ($\rho_{p,M}$) should be adjusted according to the scaling factor of the model (λ). Thus, Equation (3.6) is obtained by considering again the nearly equal kinematic viscosity between water (25°C) and liquid steel (1600°C). As a matter of example, the presence of alumina inclusions ($\rho_{p,P} = 4000 \text{ kg/m}^3$) in liquid steel ($\rho_{l,P} = 7000 \text{ kg/m}^3$) (75) establishes a density ratio of 0.6. Therefore, even if particles of 600 kg/m^3 were applied in a water ($\rho_{l,M} = 1000 \text{ kg/m}^3$) model to simulate the behaviour of inclusions, their size distribution should be corrected

by $\lambda^{0.25}$. In other words, when the model is 1:3 scale of the industrial prototype, particle sizes must be rescaled by 0.76.

$$V_r = \frac{D_P^2 g (\rho_l - \rho_p)}{18 \mu_l} \quad (3.5)$$

$$D_{p,M}^2 \cdot \left(1 - \frac{\rho_{p,M}}{\rho_{l,M}}\right) = \sqrt{\lambda} \cdot D_{p,P}^2 \cdot \left(1 - \frac{\rho_{p,P}}{\rho_{l,P}}\right) \quad (3.6)$$

However, accounting merely for the particle's natural flotation through its relative density and size may not be enough to reproduce the capture of inclusions by the bubble plume, so that the contact angle becomes another criterion to be met. A look at Table 3.1 shows that, for previously employed particles used to model bubble-induced flotation, meeting both requirements is not always possible. Also, the dispersion of non-wettable particles (high contact angle) must be carefully carried out to avoid agglomeration into coarser particles, which could disturb the measurements. For this reason, the literature suggests a pre-dispersion in a wettable solution which is also soluble in the liquid medium. For example, Jiang and Cheng (76) pre-dispersed 10 g of PE particles in ethanol and injected the suspension into the water model.

Table 3.1: Physical properties of particles to simulate inclusions.

Particle	ρ_s [kg m ⁻³]	θ [°]	Reference
Ag-coated hollow	465	40	(77)
PE	920	94	(76)
PMMA	1200	91	(78)
PS	1130	80	(79)

It is vital as well to have a reliable method for determining the concentration of particles in the system and/or the quantity of particles removed by flotation. For that, the literature proposes the current methods:

- a) High-speed camera: with a shutter speed of 1/2000s, it allows freezing particles in place to investigate mechanisms, such as the influence of the bubble wake in particle removal (76).
- b) Collecting a sample and drying it: taking into account the heterogeneity of particle concentration, aliquots are taken from the water model and, after drying out the solvent, the weight of particles is obtained (80).
- c) Coulter counter: this method also relies on aliquots taken from the water model, although particles are counted using the electric-sensing zone method. Since it is conducted in a dispersed solution, there is no need to dry the solvent (81).

Besides, some experimental setups even reproduce the slag layer using some blend of oils, such as kerosene and engine oil (80). While others rely on an overflow device to collect the floated particles from the top surface, avoiding particle re-entrainment (79,78,77).

The efforts of Tata Steel Nederland on understanding the mechanisms of bubble-induced flotation in water began in 2007 (a steelmaking company named Corus, at that time). Its onset was the work of *Stijn Klaassen* on the first steps of building and characterising a tundish water model. The first experiments on induced flotation investigated the effects of gas flow rate and water recirculation velocity on the flotation efficiency of 3M S-60 hollow glass particles (hydrophilic). Following this, *Daniël Groenendijk* (2008) made efforts to improve the water model by coupling a needle package as the bubbling device, which, compared to the previous porous brick, managed to produce a narrow distribution of bubbles around 3mm. Unfortunately, this apparatus had undergone severe corrosion over the years and was unavailable for the current work. *Fokke Zwaan* (2010) implemented an optical method to determine the particle concentration during the experiment, as the previous one relied on filtering, drying and weighing the particles after the experiment. Based on collimated light scattering by particles in suspension, the method has been applied in the following works, allowing an in-line measurement. At last, *Audrey Giffard* (2012) conducted experiments in the water model investigating the influence of two grades of polymeric particles, PMMA (hydrophilic) and PE (hydrophobic). Besides the distinct surface wettability, PMMA was denser than water (1.18 g/cm^3), so settling was a drawback affecting the results. It is also

worth mentioning the PhD thesis of *Norbert Warncke* (2014), who also investigated the attachment of particles on the surface of bubbles using a specific water model (called DABuT in his thesis) to trap a single bubble in place by a counter-flow of recirculating water so that many particles could interact with the same bubble over time. The results provided insights into how bubbles accommodate particles on their surface. However, long interaction times are not expected in steelmaking, considering the collision probability and the rising velocity. Figure 3.4 aims to display the key past efforts in a timeline, from the construction of the model through the following improvements and experiments, and the reader is advised to refer to the original reports (and thesis) for a thorough view of their work (82,83,84,85,86).

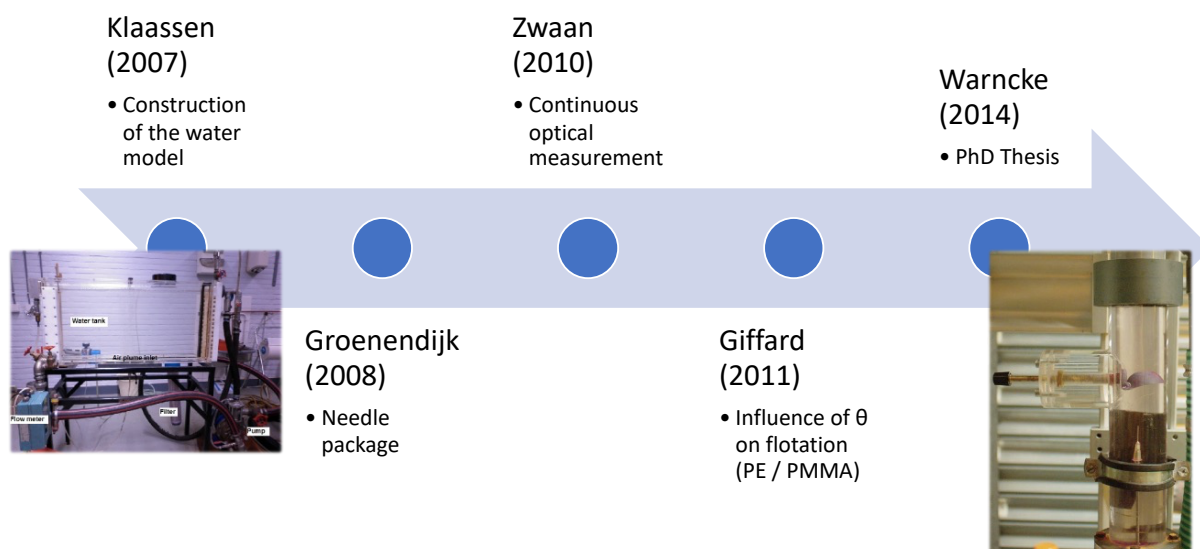


Figure 3.4: Development timeline of the tundish water model (on the left) - also depicting the DABuT facility (on the right).

Therefore, this chapter presents a design-of-experiment on a water model to assess the flotation of hydrophobic and hydrophilic particles, serving as the NMI. The particle concentration was measured over time, and the decay due to particle removal was fit to an exponential function to obtain insights into the removal rate and process efficiency.

3.3 Methodology

In order to investigate the effect of flotation on the removal of NMI, experiments were performed in a small-scale water model at the Delft University of Technology (TU

Delft). The model comprised a $1000 \times 400 \times 40 \text{ mm}^3$ vessel with acrylic walls to allow the visualisation of the experiments, as illustrated in Figure 3.5 and Figure 3.6. The system is filled with softened tap water and has a pump to recirculate the aqueous suspension and homogenise the concentration of particles. The correlation between the pump rotation (capacity percentage or rpm) and the recirculation flow rate was investigated and is presented in Figure 3.7. During the experiments, the pump was kept at 900 rpm - corresponding to a recirculating flow of 21 L/min or a velocity of roughly 22 mm/s when considering the model's cross-section. A porous bubbler was installed at the centre of the model's base, where compressed air was blown to generate bubbles in the millimetre range. In the current experiments, some similarities to tundishes operating with bubble curtains might be seen, considering the crossflow between the ascending bubble plume and the recirculating particle-containing liquid.

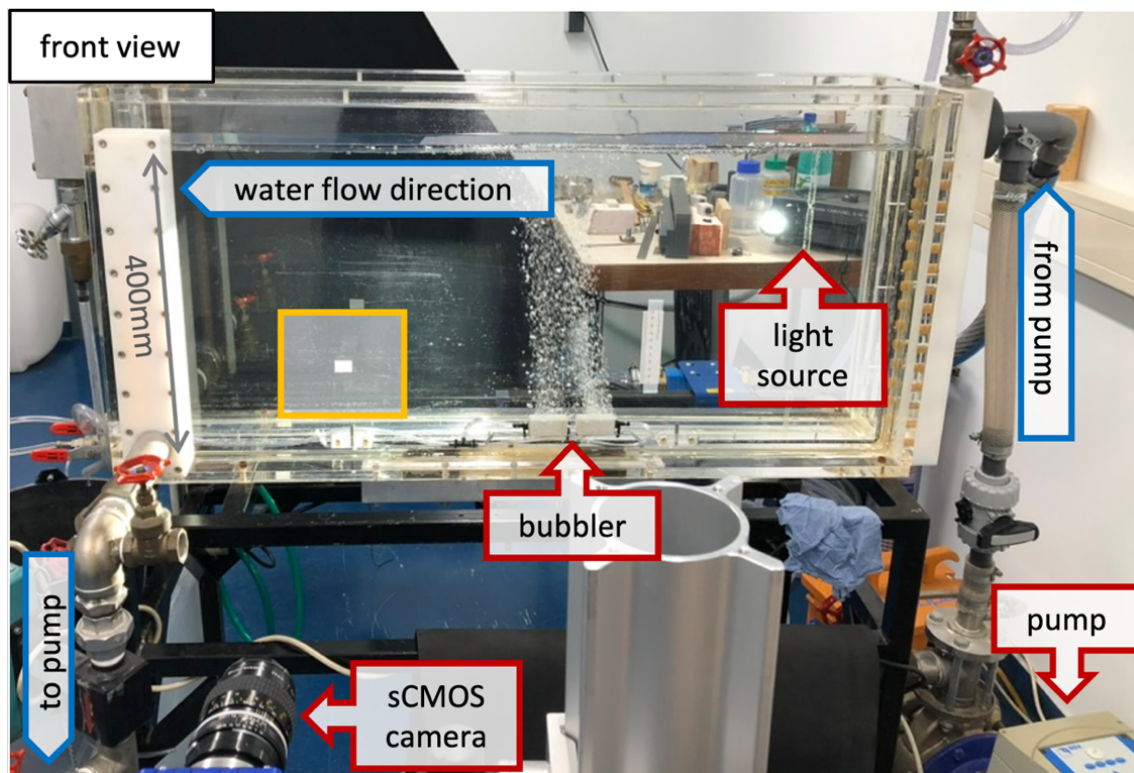


Figure 3.5: Water model's (a) front view - highlighting the recirculation path (in blue), the various apparatus (in red) and the field of view (in yellow).

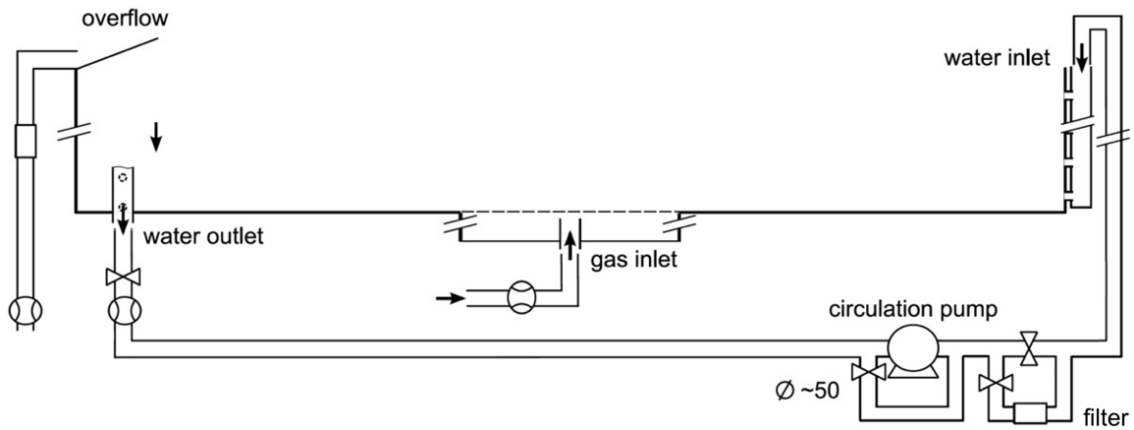


Figure 3.6: Sketch of the current water model, adapted from Stijn Klassen's report (82).

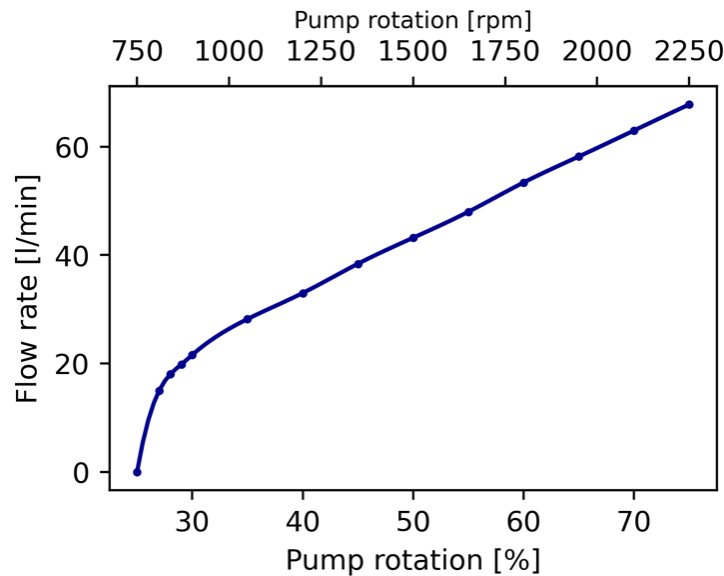


Figure 3.7: Correlation between the pump rotation (% or rpm) and the recirculating flow rate of water.

Two grades of ceramic particles with similar size distributions were selected to investigate the induced flotation of inclusions with different wettabilities. Potters Q-Cel 7014 and 3M Glass Bubbles K-20 were deployed as hydrophobic and hydrophilic particles, respectively (87,88). Both were spherical glass hollow spheres, with a density lower than that of water (0.14 and 0.20 g/cm³, respectively). From the Stokes Law (89) in Equation (3.5), the terminal velocity of a buoyant particle (V_T) is directly proportional to the square of the particle diameter (D_P). Also, it depends on the gravitational acceleration (g), the density of both the solid (ρ_s) and the liquid (ρ_l), and the fluid's

dynamic viscosity (η). Consequently, sieving the particles before the experiment is an alternative to control the natural flotation of particles, allowing the influence of bubble-induced flotation to be measured. Considering that the particle density is directly related to the ratio between its glass thickness layer and the hollow bulk, one could expect that smaller particles have a higher density, approaching the solid glass one. Therefore, the particles were dry-sieved below 220 μm to remove the agglomerates, dispersed on a 3:2 water-isopropanol solution and wet-sieved below 75 μm , as represented in Figure 3.8. After this procedure, roughly 30% of the initial mass of particles was in the produced suspension.

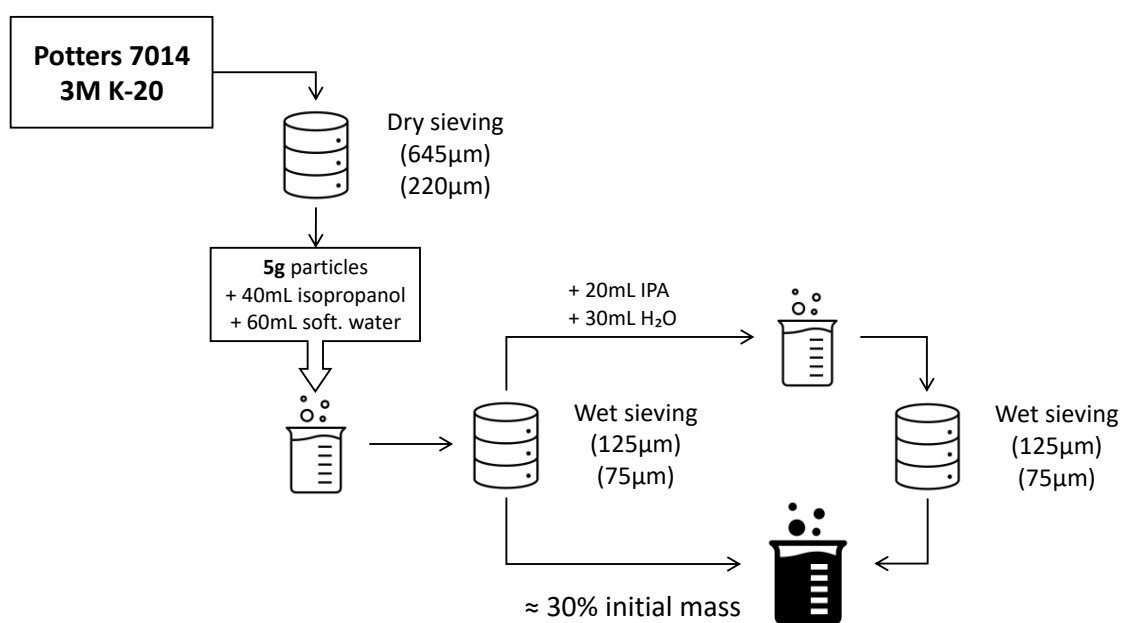


Figure 3.8: Flowchart of the suspension's preparation considering the sieving steps.

The particles (as received) and the obtained suspensions were characterised in a Malvern Panalytical Mastersizer 2000 to get their size distribution, coupled with a Hydro 2000S sample dispersion unit. In these analyses, the solvent phase was ethanol 96% v/v for the hydrophobic particles and deionised water for the hydrophilic ones. All samples were analysed according to Fraunhofer's theory of light scattering (90). The particle grades were characterised by their size distribution before and after the wet-sieving procedure to assert that hydrophilic and hydrophobic particle grades have similar granulometry. The size distribution results are presented in Figure 3.9, based on which one can notice the similarity in size distribution between the hydrophilic and hydrophobic grades. It is also

possible to infer that the sieving procedure not merely removed particles above 75 μm but generated a new distribution of smaller particles. For the hydrophilic grade, the values of d_{10} , d_{50} and d_{90} (see Table 3.2) were cut down to two-thirds, whereas these values decreased by roughly half for the hydrophobic one.

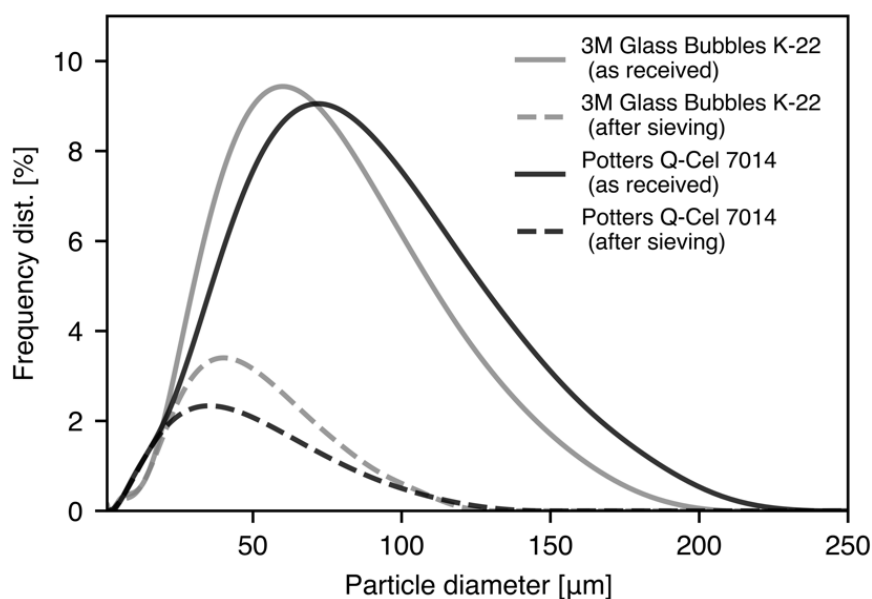


Figure 3.9: Particle size distribution obtained by a Malvern analyser before and after the wet-sieving procedure.

Table 3.2: Particle diameters measured from their size distribution before and after the wet-sieving procedure.

Sample		d_{10} [μm]	d_{50} [μm]	d_{90} [μm]
as received	3M K-20	21.6	51.1	100
	Potters 7014	20.2	57.6	114
in suspension	3M K-20	14.2	34.2	66.1
	Potters 7014	10.1	28.5	64.3

SEM micrographs were obtained by a TESCAN MIRA microscope under high vacuum, using the secondary electron mode with an acceleration voltage of 25kV, a working distance of 15 mm and a beam current of 300 pA. Samples were coated with a 10nm layer of AuPd alloy. The micrographs in Figure 3.10 (a-d) show that the particles

are perfectly round, and few fragments and debris are observed in the samples before sieving. There is a noticeable decrease in average particle size after wet-sieving and preparing the suspensions, which attests to the results in Figure 3.9. However, small fragments of broken particles were also among the sieved fraction that was suspended, and the debris would tend to sediment during the experiments.

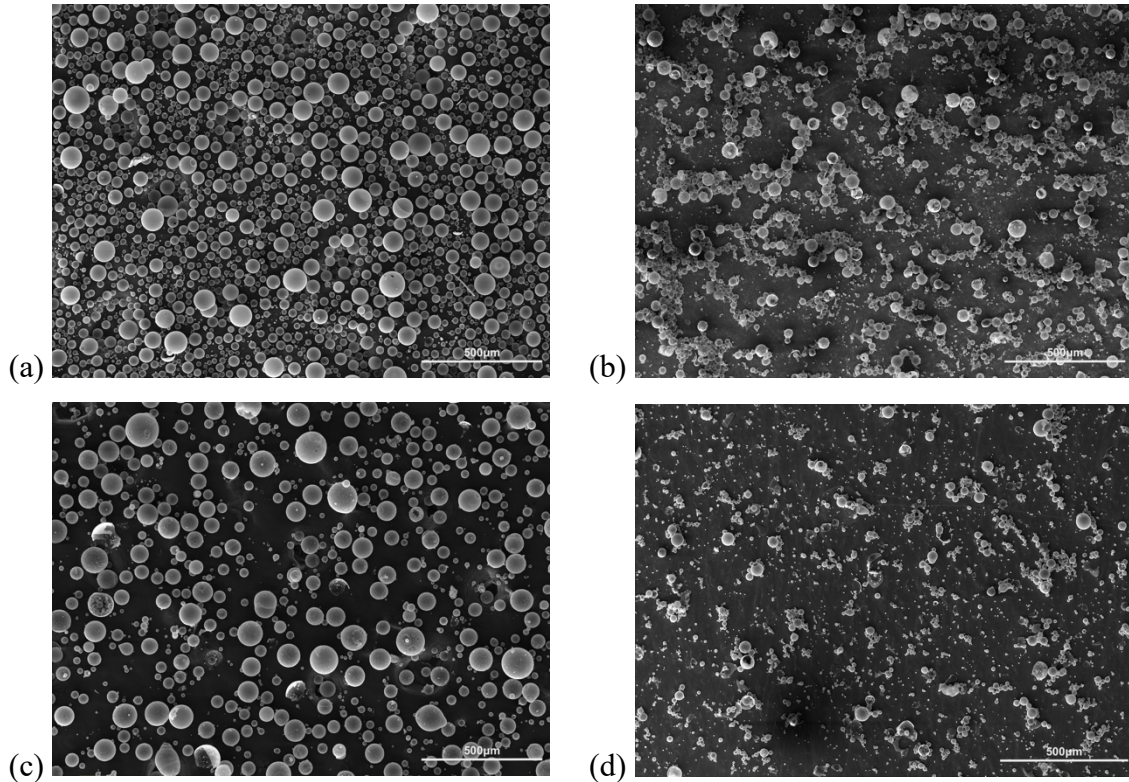


Figure 3.10: Micrographs of (a,b) hydrophilic and (c,d) hydrophobic particles, before and after wet-sieving, respectively.

During the flotation experiments, the concentration of particles was indirectly measured by a light scattering technique, as represented in Figure 3.11a. A 250-watt tungsten-halogen lamp, located in the back part of the model, was used as a source of collimated light. The light rays are scattered by the particle and collected by an sCMOS camera (LaVision Imager) in front of the model at 1 Hz, as in the example of Figure 3.11b. The camera has a Nikon 55 mm lens installed at full aperture ($f/2.8$). Each frame has 2160x2560 pixels, is 16-bit deep and corresponds to a 1 ms exposure time. The advantage of this inline technique is the continuous measurement of particle

concentration by averaging the light intensity over an area (highlighted in yellow in Figure 3.5a).

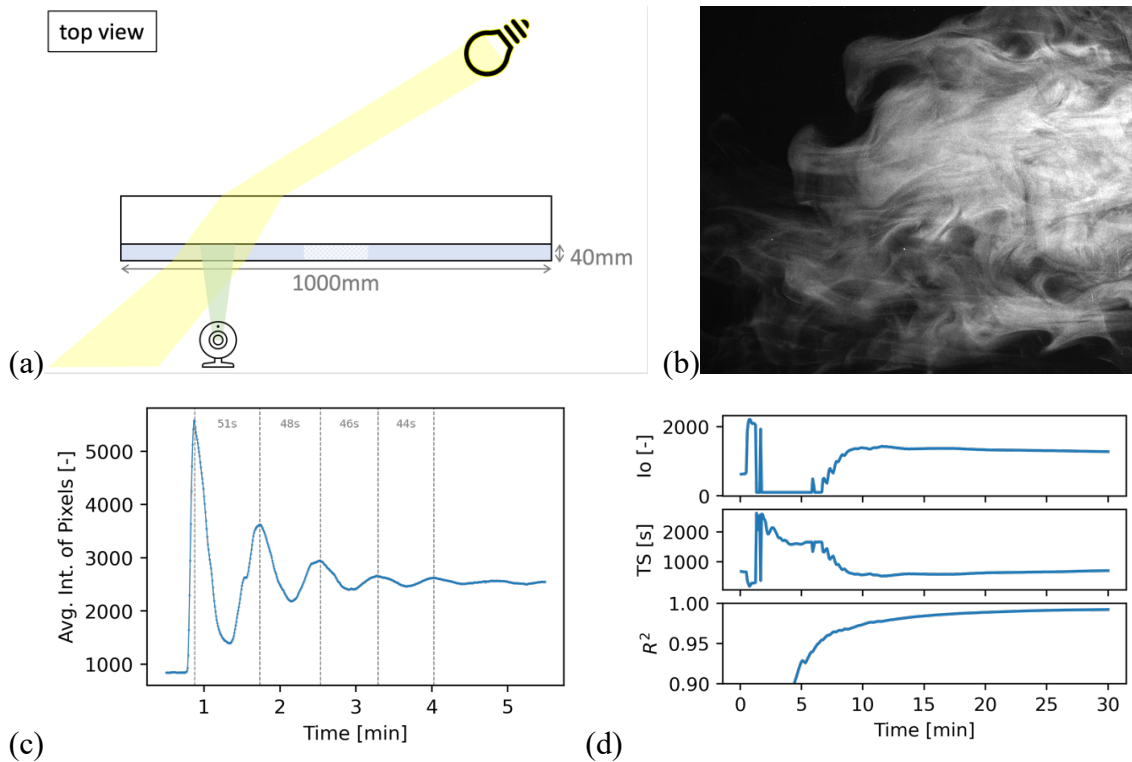


Figure 3.11: (a) Water model's top view – illustrating the light scattering system (b) Example of a frame captured by the sCMOS camera right after particle injection, (c) the light intensity highlighting the homogenisation of particles due to recirculation and (d) the parameters of the exponential fit (TS and I_0) as a function of the measurement time.

The experiment consisted of (summarised in Figure 3.12):

- Measuring the initial background light intensity while injecting the same gas flow rate as given in the experiment to account for the influence of bubbles in the scattered light;
- 5 minutes of homogenisation after injecting 80 mL of the particle suspension close to the water outflow (as seen in Figure 3.11c, it takes approximately 50 seconds for each cycle of particle recirculation and 5 minutes for the concentration to be stable enough for the measurements);
- 10 minutes of natural flotation, i.e., without injecting gas, as the parameters related to the exponential fit (which will be later introduced in this report) are

significantly varying before 10 minutes, corroborated by the low value of R -squared in Figure 3.11d;

- d) 25 minutes of combined flotation (i.e., natural + induced flotation) - when the mechanisms induced by the bubble plume were coupled by injecting compressed air through the porous bubbler.
- e) A step of filtering out particles, to ensure that the background did not change throughout the measurement.

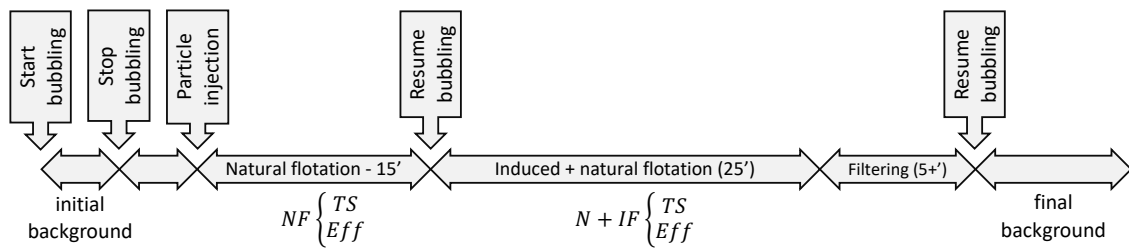


Figure 3.12: Summary of the steps and times for the flotation experiments.

Besides, it is essential to mention that the scattered light intensity, as measured by the sCMOS camera, is subject to variations in the light source, as seen in the black curve of Figure 3.13a, where oscillations and shifts in the data are present. Thus, the strategy to overcome this issue was to normalise the light intensity by the light source's power. Ideally, two cameras would be required to get both intensities. However, due to the available equipment, an alternative was explored by glueing white stickers to the front and back walls of the water model (Figure 3.13b). As the white stick scatters most of the irradiated light, its intensity is less disturbed by the particle concentration, as it works as a suitable normalisation. From the grey curves of Figure 3.13a, it is noticeable how stable the signal becomes after the normalisation, mainly when the sticker at the front wall is considered. Thus, this setup was chosen for the experiments, and an example of the measured frame with the white stick at the very centre is seen in Figure 3.13c.

The light intensity along the steps of flotation ("b" and "c") was fitted by an exponential decay function over time (t), as in Equation (3.7), from which the time scale (TS) is directly obtained (91). The final efficiency is calculated as $Eff = \frac{I_{\infty}}{I_{\delta} + I_{\infty}}$, where I_{∞} and I_{δ} represent the intensity at an infinite time and the decrease from the initial value, respectively. At this point, it is crucial to understand how these two parameters are related

to the performance of the porous bubbler in removing inclusions. The maximum value that could be achieved for the percentage of removed particles is called “efficiency”, which does not depend on the removal rate, as this property is obtained by extrapolating to an infinite time. Oppositely, the time scale (TS) represents the mean lifetime of particles in suspension, which is inversely related to the removal rate and indicates how fast the maximum efficiency is reached. In summary, the overall performance of a purging bubbler depends on this pair of parameters, and high efficiencies with low time scales are desired so that a large number of inclusions is removed in a short time.

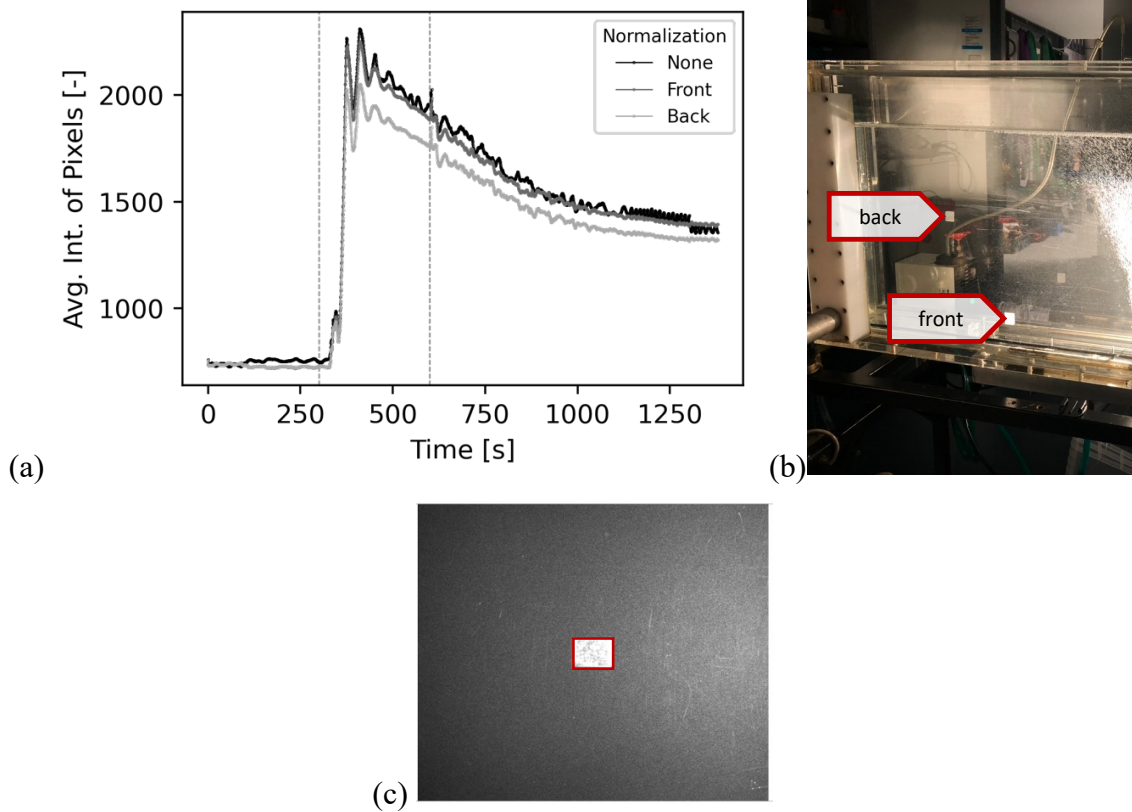


Figure 3.13: (a) The corrected light intensity when normalising it by the light source from white stickers at (b) the front and back walls of the water model and (c) the resulting frame (20x17cm).

$$I(t) = I_{\delta} \cdot \exp(TS^{-1} \cdot t) + I_{\infty} \quad (3.7)$$

The system has been calibrated within the analysed range (up to 6500 counts), showing a linear correlation to the particle concentration. The calibration was conducted by injecting

the same volume of a homogeneous particle suspension four times, as in Figure 3.14a. When collecting these results, as in Figure 3.14b, the light intensity is well fitted by a linear correlation (R-squared value of 0.9965), allowing the light intensity to be directly correlated to the particle concentration. Thus, after fitting the intensity curve by the exponential decay, the initial value ($I_{t=0}$) is taken as 0% of removed particles and the background measurement as 100%, so the intensity recorded by the sCMOS camera may be converted into particle concentration in percentage.

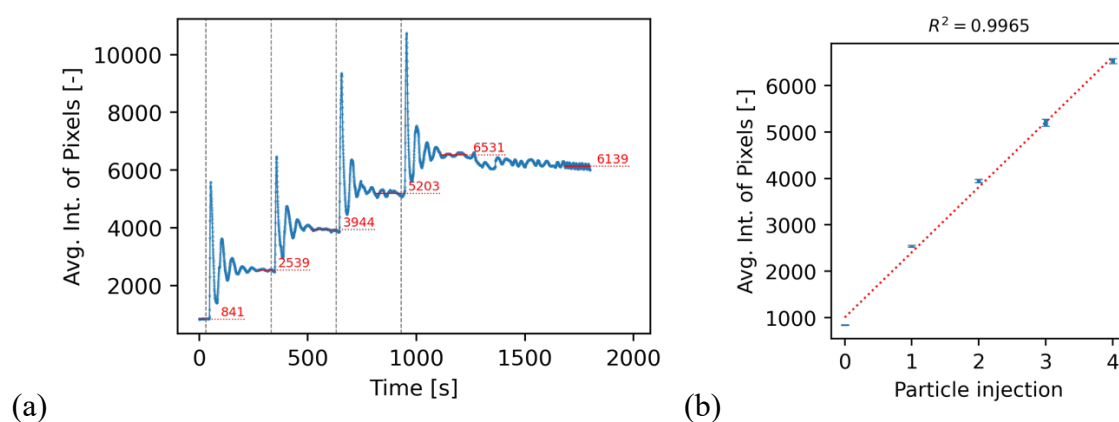


Figure 3.14: (a) Calibration experiment with four injections of particle suspension and (b) the linear correlation between light intensity and particle concentration.

3.4 Results and discussion

The sieved suspension of hydrophobic particles was used in the flotation experiment, and the results are shown in Figure 3.15, which presents the percentage of removed particles as a function of time. The first increase of particle removal represents the particles' natural flotation as no gas bubbles were being injected into the system, and the exponential fitting (dashed red line) shows that the particle concentration tends to an efficiency of 43.1% at an infinite time. However, the aspects regarding natural flotation are addressed in the next chapter, as the current one focuses on comparing hydrophilic and hydrophobic particles. After 10 minutes, bubbles started to be injected into the system, leading to an instantaneous increase in light scattering due to tiny bubbles in the camera's field of view, which tend to float straightaway. Then, the flotation sped up as the TS (time scale) parameter was reduced from 663 to 474 seconds (i.e., a 40% faster

removal), and the efficiency increased to 65.2% (1.63 times the one for plain natural flotation) as the mechanisms of induced flotation were coupled by the bubble plume.

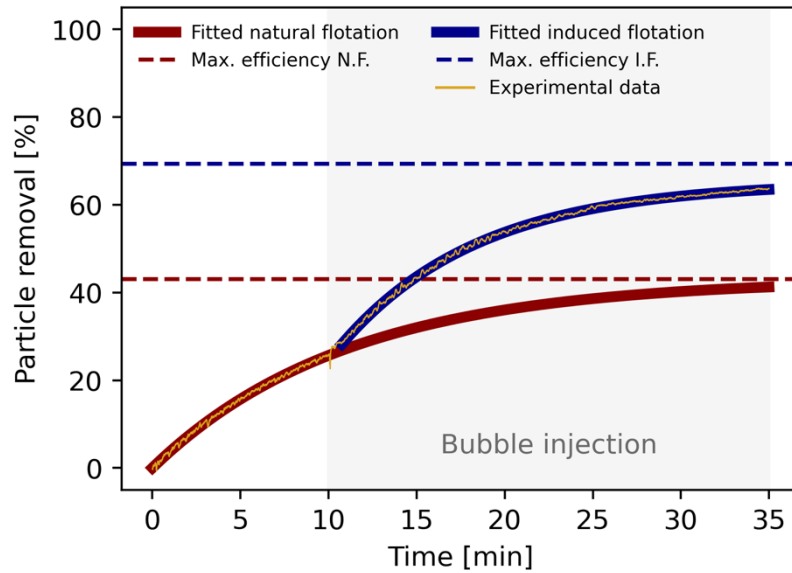


Figure 3.15: Particle removal as a function of time for the flotation experiment with hydrophobic particles ($Q_g = 25$ L/h).

The experiment with hydrophobic particles highlighted the higher removal rate and efficiency when bubbles were injected. However, the three mechanisms of bubble-induced flotation (i.e., surface attachment, wake capture and flow-induced removal) simultaneously contribute to this result, making it impossible to determine their share. Thus, the same experiment was carried out with the sieved suspension of hydrophilic particles, aiming at coupling the surface attachment mechanism, and the results are presented in Figure 3.16. During the natural flotation step, the exponential fitting led to a TS parameter of 727 seconds and an efficiency of 59.1%. Conversely, to the previous experiment, the injection of bubbles initially led to a slight increase in the scattered light, as indicated by the decrease in particle removal in Figure 3.16a. This effect might be related to the re-entrainment of particles from the top surface of the system as the bubble plume locally increases the instability of this layer. It is clear from Figure 3.16b-d that an increase in the gas flow rate intensifies the re-entrainment of particles, even reaching a value close to 0% for 150 and 200 L/h. Thus, the results of high gas flow rates are not compared in this report as they are deeply affected by the particle re-entrainment.

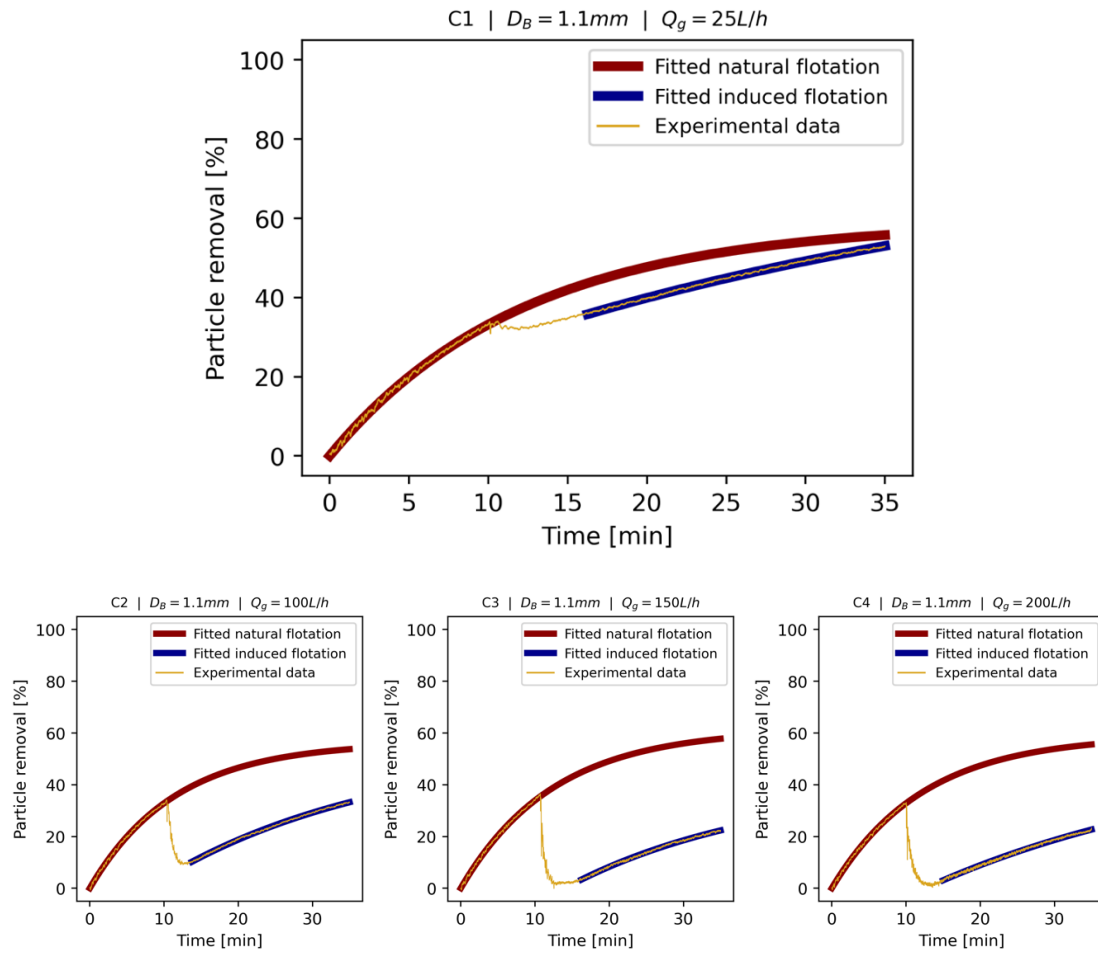


Figure 3.16: Intensity of scattered light as a function of time for the flotation experiment with hydrophilic particles for gas flow rates of 25, 100, 150 and 200 L/h, highlighting the particle re-entrainment after bubble injection starts.

Considering the gas flow rate of 25L/h in Figure 3.16a (comparable to Figure 3.15 for the hydrophobic particles), it is worth noting that particle re-entrainment dominates the first minutes of induced flotation and, after 6 minutes of gas injection, the balance between particle removal and re-entrainment came to a stable condition, allowing an exponential equation to fit the results. Although the removal rate decreased 2.1-fold, with TS moving from 727 to 2264 seconds, the efficiency increased to 86.2% when induced flotation mechanisms were coupled. Thus, compared to the results for hydrophobic particles, the bubble injection led to a smaller increase in the maximum efficiency (1.46

times the natural flotation's one against 1.63) but a much longer removal time, even slower than the natural flotation.

From the mechanisms of induced flotation, one could expect a higher efficiency increase for the hydrophobic particles when compared to the hydrophilic ones, as the attachment to the bubble surface is unlikely to occur. Besides, the removal rate sped up in the experiment of non-wettable particles, indicating that bubble injection should start as soon as possible during the liquid metal refining step. On the other hand, the induced flotation of wettable particles increased efficiency while decreasing the removal rate, showing that gas purging too early in the process could lead to a delay in the removal of non-metallic inclusions.

Regarding the re-entrainment of hydrophilic particles when the bubble plume was started, the instability of the floated particles layer at the water model's top region may be related to the thermodynamics of capturing particles at liquid-gas interfaces. As shown in Figure 3.17, the change in energy due to the attachment depends on the macroscopic contact angle (θ_{slg}) among the solid, liquid and gas phases, defining three scenarios:

- i. Non-wettable particles (90° or higher) show a negative ΔE_{att} , causing the detachment barrier to be higher than the attachment one ($\Delta E_a < \Delta E_d$). Thus, particles are stable at the liquid-gas interface, as in the experiment with hydrophobic particles (Figure 3.15);
- ii. Slightly wettable particles (around 60°) can still be attached to the liquid-gas interface because a local minimum energy point is observed beyond the attachment barrier. However, it represents a meta-stable condition as ΔE_{att} is positive (and $\Delta E_d < \Delta E_a$), causing the particle to detach and return to the liquid phase easily;
- iii. Highly wettable particles (30° or lower) do not even have a metastable condition of attachment, and the energy components (ΔE_{att} , ΔE_d and ΔE_a) are not applicable.

Considering that the hydrophilic grade of particles (3M Glass Bubbles K-20) was made of soda-lime-borosilicate glass with no surface treatment to change their hydrophilicity, one could expect a low macroscopic wetting angle in contact with aqueous solutions and, therefore, a condition close to the third scenario – where particles are not stable at the liquid-gas interface. Thus, the naturally floated particles remained at the

model's top surface merely because of their low density (compared to the water phase) and re-entrained the system when the bubble plume started, increasing the turbulence of the top layer. On the other hand, the additional flotation mechanisms - related to either the particles captured by the bubble wake region or by the induced flow pattern – would still be activated, which explains the higher efficiency of removal when bubbles were injected (Figure 3.16). Therefore, changes in the system to remove the floated hydrophilic particles right after reaching the top layer would be required for future experiments so that it can suitably act as a slag layer (80).

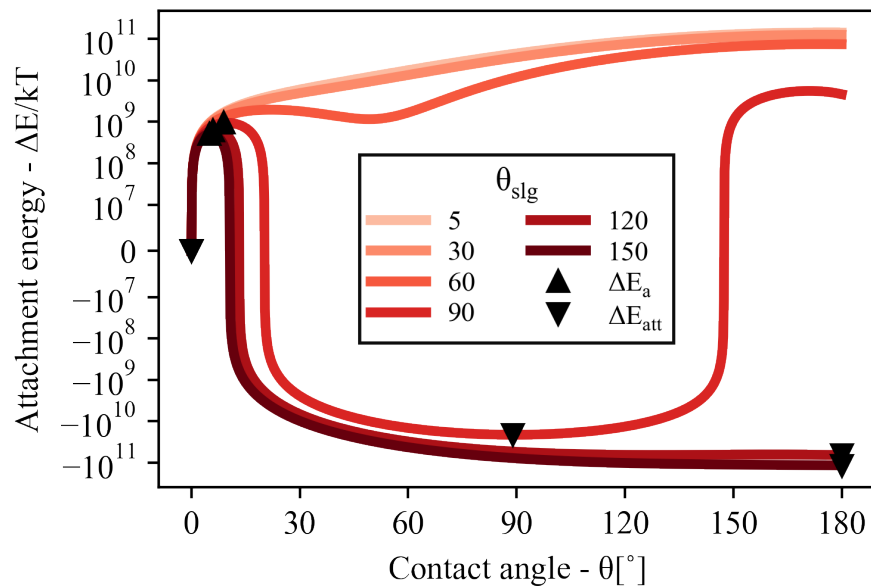


Figure 3.17: Change in energy due to the attachment of a particle at a liquid-gas interface as a function of its position for different values of macroscopic contact angles (θ_{slg}). Obtained as described in (17) considering hypothetical values of liquid-gas tension ($\gamma_{lg} = 72.8 \text{ mJ/m}^2$), line tension ($\gamma_{slg} = 0.3 \text{ } \mu\text{J/m}^2$), bubble size ($D_B = 1 \text{ mm}$), particle size ($D_P = 50 \text{ } \mu\text{m}$) and contact angle (θ_{slg}).

3.5 Conclusion

This chapter analysed the flotation behaviour of hydrophobic and hydrophilic hollow glass particles by conducting experiments on a water model and measuring the particle concentration by a light scattering technique. Particles were pre-dispersed in an isopropanol-water solution and wet-sieved to generate inclusion-like suspensions. The

natural flotation of both particles presented a similar removal rate. When 1.1 mm bubbles were injected, the removal rate for hydrophobic particles increased by 40%, and the removal efficiency was 1.63 times the natural flotation's efficiency. Conversely, the bubble plume caused a 2.1-fold decrease in the removal rate of hydrophobic particles, although the efficiency was 1.46 times the natural flotation one. During this latter experiment, the naturally floated hydrophilic particles re-entrained from the model's top region as bubbles were injected. Such an effect was expected as these particles are highly wetted by the liquid and not captured by the liquid-gas interface due to their low contact angle.

CHAPTER 4 – BUBBLE PLUME EFFECTS ON THE FLOTATION KINETICS OF NON-METALLIC INCLUSIONS BASED ON EXPERIMENTAL OBSERVATIONS

4.1 Introduction

Following the discussions in Chapter 2 on the role of surface wettability in determining the bubble size in the plume and the design of a reliable experimental procedure for flotation experiments in Chapter 3, this chapter investigates how bubble size and gas flow rate influence the kinetics of induced flotation. By applying an exponential decay fit to particle concentration, the removal rate (by the specific time of decay) and the maximum efficiency were determined, enabling comparisons of different bubbling conditions. The optimal gas flow rate was found to be around 385 L/min/m² - equivalent to 30 NL/min, for a 900x100 mm² purging beam in the tundish. Additionally, bubbles within 0.7–1.6 mm showed faster removal rates, while those within 0.2–1.4 mm achieved the highest removal efficiencies. These findings were compared with industrial bubbling practices in the tundish, emphasising its significance for producing clean steels.

4.2 Literature review

There is a vast body of literature on the origins, reactions and effects of non-metallic inclusions (NMI) in steelmaking (13,92,10) and, depending on their size and concentration, they might deeply affect the mechanical properties of high-performance steels. The classical stress-life (SN) curve is used for low- to high-cycle fatigue and shows a stress limit below which the material has theoretically infinite life. However, the Wöhler diagram was deduced for surface defects, such as cracks and surface roughness, not considering the effect of internal fragile inclusions in the metallic matrix (93). For structural components working on fatigue regimes beyond 10⁸ cycles (very high and ultra-high fatigue), sub-surface mechanisms contribute to premature failure, dismantling the concept of a stress limit for an infinite life (94), as in Figure 4.1. Therefore, “clean steel” is defined as a condition where non-metallic inclusions do not decrease the in-service properties of the metallic part (12), displaying, therefore, a strict correlation to the steel’s application, as there is no “inclusion-free” grade.

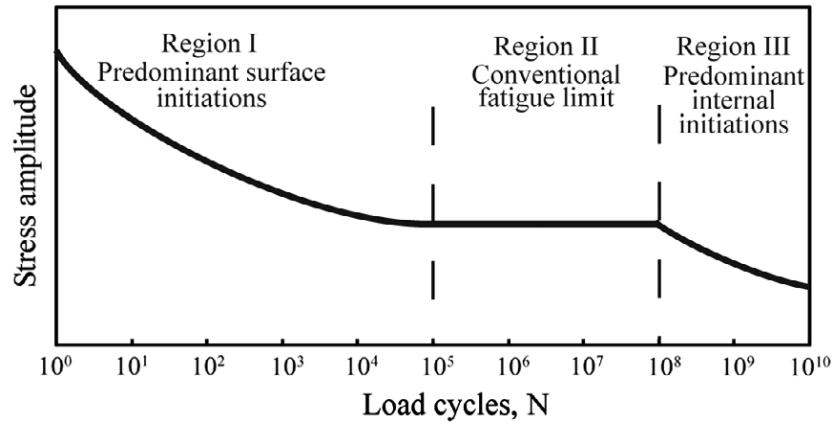


Figure 4.1: The S-N curve (or Wöhler diagram), highlighting the contribution of non-metallic inclusions above 10^8 cycles (93).

Aiming at determining the optimum conditions to withdraw non-metallic inclusions from liquid metal effectively, efforts to define the optimum bubble size range were made based on the total probability of inclusion removal by bubble attachment, i.e. mechanism “A” in Figure 3.2. As represented in Equation (4.1), the total probability comprises those of bubble-particle collision (P_C), adhesion (P_A) and detachment (P_D). It is worth noting that, for this latter term, a lower detachment probability increases the overall removal (26).

$$P = P_C \cdot P_A \cdot (1 - P_D) \quad (4.1)$$

The individual probabilities are analysed in Figure 4.2:

- a) The collision probability is determined by the interception of bubble and particle trajectories. Thus, a plume of smaller bubbles increases P_C , whereas larger inclusions are more readily found in the liquid metal. Even so, one might notice in Figure 4.2a that the probabilities for 0.1 and 10mm bubbles to collide with 5- μm inclusions are around 0.45% and 0.003%, respectively. This range highlights the challenge of removing micro-sized inclusions from the molten bath (26).
- b) Following the collision, the particle slides over the bubble surface and relies on liquid film drainage to be truly captured, thereby defining the adhesion

probability. For inclusions of 5 to 10 μm , P_A is relatively high and almost independent of bubble size, as in Figure 4.2b. However, inclusions of 20 μm or larger exhibit an interesting behaviour in adhesion probability: bubbles below 2 mm have a low rising velocity, thus increasing the sliding time, and bubbles larger than 3 mm increase the sliding length due to their longer perimeter (95).

- c) Finally, the attached particle must be brought to the slag layer without detaching back to the liquid metal. An indicator of this probability is the particle's position at the bubble interface, so that the flow stream may detach more exposed particles. Thus, as shown in Figure 4.2c, bubbles below 0.5 mm tend to accommodate a smaller portion of the inclusion, increasing P_D .

Based on the individual probabilities, Wang *et al.* (95) discuss that the likelihood of collision and adhesion is maximised when bubbles are smaller than 2.0 mm, whereas the detachment probability increases for bubbles below 0.5 mm. Thus, an optimum bubble size range between 0.5 and 2.0 mm is typically pursued for ceramic refractory devices aiming at steel cleanliness. Complementarily, it is reported that bubble shapes other than the spherical one can lead to an increase in particle removal due to the wake zone (mechanism “B” in Figure 3.2) - i.e., when the bubble becomes large enough to shape it into a spheroid or a spherical cap (15).

With these concepts in mind, the goal of producing “clean steels” becomes a challenge when designing porous ceramic refractories to fulfil the requirement of bubble sizes within the optimum range. Typically, inert gas is injected into the ladle during the secondary refining through devices known as purging plugs (21). These devices operate in a wide range of gas flow rates (usually from 50 to 200 NL/min) as their role in the ladle is not merely the removal of non-metallic inclusions but also the injection of gas to allow the chemical and thermal homogenisation of liquid melt (mainly during the alloying step) and the formation of the slag’s “open eye”, exposing the liquid metal to the environment for additives to be incorporated (65,96). Additionally, the gas injection is intermittent as the ladle is constantly moved by cranes at the steelmaking plant, leading to periods of liquid metal infiltration into the porous structure (38), as seen in Figure 4.3. Therefore, the steel ladle might not have the best conditions to bear a porous device tailored to remove non-metallic inclusions (NMIs).

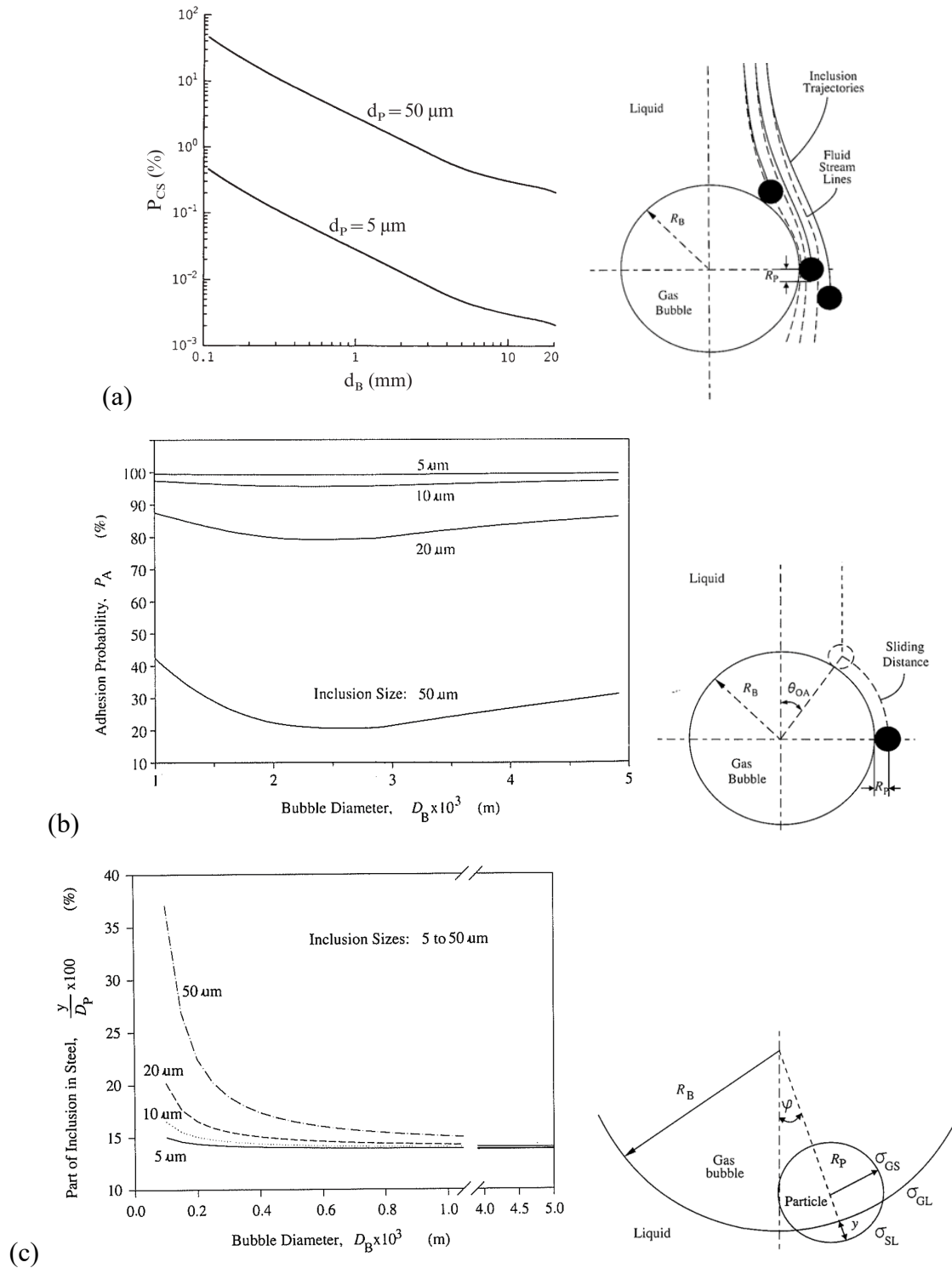


Figure 4.2: Individual probabilities of (a) collision, (b) adhesion and (c) detachment, adapted from (95,26).

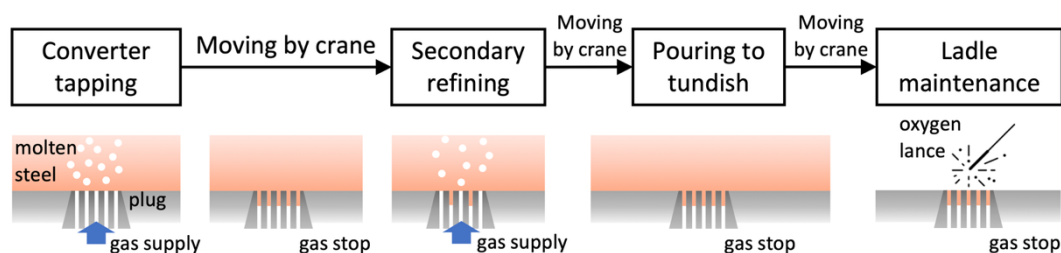


Figure 4.3: Schematic representation of the infiltration and cleaning cycle in porous plugs, adapted from (97).

The results from Chapter 2 have already shown the importance of the plug's surface wettability in generating bubbles, where high contact angles with the liquid cause the bubble to spread over the bubbler, thereby increasing its equilibrium diameter and facilitating detachment. Under these conditions, the effect of the pore diameter on the bubble size might even be hindered. On the other hand, designing a porous structure with a low contact angle (highly wettable) and larger pore size to also allow the injection of low-to-high gas flow rates is not a good alternative when aiming at controlling the infiltration of liquid metal, as the only controllable variable would be the gas counterpressure (38). Despite the efforts to keep a gas buffer to slow down the plug's infiltration (97), this solution might face practical issues, as a pressured gas container must be installed in the ladle's outer shell. In this scenario, the tundish emerges as a "more than a buffer" vessel where the conditions for the flotation of small inclusions are fulfilled (98). Correlating to previously discussed requirements, the tundish allows a constant injection of gas along its life span, reducing the infiltration of liquid metal and even making the application of wettable compositions possible. Besides, there is no requirement for high gas flow rates as alloying is not conducted in the tundish, and thus, a porous structure may be designed to focus on inclusion removal. Commercial solutions for injecting gas in the tundish are currently available, as in Figure 4.4, consisting of magnesia porous bricks operating with gas flow rates of 10 to 60 NL/min (99).

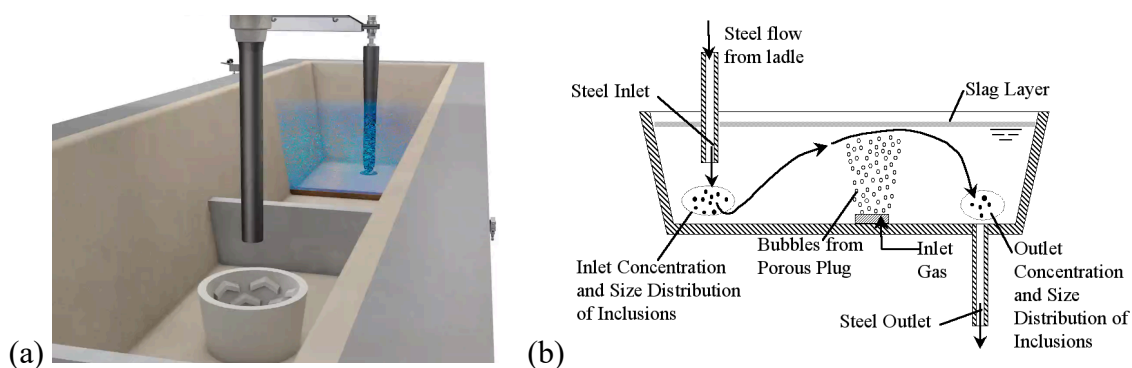


Figure 4.4: Representations of a purging beam creating a bubble barrier for inclusions (99,100).

Focusing on the influence of the bubble size distribution and gas flow rate on the kinetics of particle's flotation, the authors conducted experiments on a water model with two porous structures to generate the bubble plumes in a quasi-2D recirculating water tank. Hydrophobic glass hollow particles were applied to simulate the behaviour of non-metallic inclusions, and their concentration was indirectly measured by light scattering and fitted by an exponential decay. Unlike other works from the literature (70,80,75), the aim of the present one is not to reproduce a specific industrial tundish setup, but to gain experimental insights into the influence of the bubble plume on the efficiency and characteristic time for the removal of NMIs.

4.3 Methodology

This work made use of a water model (as described in Chapter 3) to conduct the physical simulations of induced flotation. It consisted of a 1000 x 400 x 40 mm³ vessel, filled with softened tap water and coupled with a system to homogenise the concentration of particles during the experiment. The behaviour of non-metallic inclusions was reproduced by glass hollow spheres (Potters Q-Cel 7014), following a procedure to sieve them to a size distribution between 10.1 and 64.3 μm (d_{10} and d_{90} , respectively). The nature of these particles provided the indirect measurement of their concentration using a light scattering method, where a scientific camera (LaVision VC-Imager sCMOS CLHS) recorded the scattered rays at 2 Hz and an exposure time of 1 ms. The experiment consisted of (a) 5 minutes of homogenisation after injecting 80 mL of the particle suspension, (b) 10 minutes of natural flotation - without injecting gas, (c) 25 minutes of

combined flotation - when the mechanisms induced by the bubble plume were coupled, and (d) a step of filtering out particles to ensure that the background did not change throughout the measurement. More details of the experimental setup are available in a previous publication by the authors (101).

The light intensity along the steps of flotation (“b” and “c”) was fitted by an exponential decay function over time (t), as in Equation (3.7), from which the time scale (TS) is directly obtained. The final efficiency is calculated as $Eff = \frac{I_{\infty}}{I_0 + I_{\infty}}$, where I_{∞} and I_0 represent the intensity at an infinite time and the decrease from the initial value, respectively. At this point, it is crucial to understand how these two parameters are related to the performance of the porous bubbler in removing inclusions. The maximum value that could be achieved for the percentage of removed particles is called “efficiency”, which does not depend on the removal rate, as this property is obtained by extrapolating to an infinite time. Oppositely, the time scale (TS) represents the mean lifetime of particles in suspension, which is inversely related to the removal rate, and indicates how fast the maximum efficiency is reached. In summary, the overall performance of a purging bubbler depends on this pair of parameters, and high efficiencies with low time scales are desired so that a large number of inclusions is removed in a short time.

Industrially speaking, the gas injection in the tundish is typically controlled in the normal litre per minute range (NL/min). However, the actual volume of gas released by the porous structure is affected by temperature and pressure differences from the standard conditions and by the area of the porous bubbler. Thus, by applying this assumption when using purging beams, the corresponding value in L/min/m² may be obtained, representing the volume of gas injected per square meter - also referred to as the linear velocity of the gas at the outlet, as the dimensional analysis of the units will lead to “Length/Time” (102).

To carry out this procedure, the standard flow rate is converted to the actual gas flow rate on the porous surface in Equation (4.2) by assuming an ideal gas behaviour and considering the temperature and pressure difference from the standard conditions (T_{std} and P_{std} , respectively) to the conditions at the gas outlet (T_{gas} and P_{gas}).

$$Q_g = Q_{g, std} \cdot \frac{P_{std}}{T_{std}} \cdot \frac{T_{gas}}{P_{gas}} \quad (4.2)$$

The values at 273 K (0 °C) and 101.325 kPa (1 atm) may be directly applied in Eq. (4.2) for T_{std} and P_{std} , respectively, whereas some other aspects must be discussed for T_{gas} and P_{gas} . For the temperature, the gas is typically heated up to the temperature of the vessel's outer shell (around 300 °C, or 573 K), whereas the pressure at the gas outlet is the atmospheric plus the ferrostatic one. Assuming a 1m-high column in the tundish (H_l) of liquid steel with a density of 7000 kg/m³ (ρ_l), the linear velocity of the gas (U_g) is derived by Equation (4.3), where " A_{PB} " is the area of the purging beam and " g " the gravitational acceleration.

$$U_g = Q_{g,\text{std}} \cdot \frac{101325 \text{ Pa}}{273\text{K}} \cdot \frac{573\text{K}}{101325 \text{ Pa} + \rho_l g H_l} \cdot \frac{1}{A_{\text{PB}}} \quad (4.3)$$

As mentioned, the typical range for the gas flow rate in a purging beam of 900 x 100 mm² is within 10 to 60 NL/min. Substituting these values into Equation (4.3), the corresponding gas flow rate per area is expected within the 140 to 830 L/min/m² range. Two porous structures were applied to simulate this condition in the water model: a pair of commercial air diffusers (AD) and a porous ceramic brick (PB). A calibrated flow meter of 25 to 250 L/h measured the gas flow rate injected through these bubblers. As summarised in Table 4.1, the nine experiments discussed in this report comprised six levels of gas flow rates applied to the porous brick and only three to the pair of air diffusers. Although higher gas flow rates would still be within the range of interest, the reason behind this choice is that the air diffuser generated smaller bubbles. Thus, its plume remained in the recirculating flow pattern for gas flow rates higher than 75 L/h, scattering more light to the camera and disturbing the measurement of the particle concentration.

Figure 4.5 summarises the correlation between the gas flow rate applied to the purging beam in the tundish and to the bubbler in the water model. It highlights that the experimental conditions of the conducted tests are within the industrial range - except for experiment "B1," which falls below the lower limit. The choice for testing two porous bubblers aimed at generating different bubble size distributions. Thus, the bubble plumes for the nine experimental conditions were characterised by a shadowgraphy technique, where an LED panel (9x16 in², roughly 23x41 cm², from Edmund Optics) was placed behind the water model, and the sCMOS camera captured the shadow generated by the

bubbles (103). The recorded frames were analysed by an algorithm in Python using the OpenCV library (*cv2*), as presented in Figure 4.6.

Table 4.1: Experimental conditions of the measurements conducted in the water model.

	Bubbler	Bubbler area $A_{mo} [m^2]$	Gas flow rate $Q_g [L/h]$	Flow rate per area $U_g [L/min/m^2]$
A1	Pair of air diffusers	0.00250	25	170
A2			50	330
A3			75	500
B1	Porous brick	0.00435	25	95
B2			50	190
B3			75	290
B4			100	380
B5			150	580
B6			200	770

The pipeline of image analysis consisted of the following:

- Binarising the images of the bubble plumes based on a threshold value (*cv2.threshold* function). However, after this step, the bubble centre tends to have the same shade as the background.
- Filling the holes inside the bubbles, starting from a seed pixel outside any bubble and connecting it to the neighbouring pixels until the whole background is mapped (*cv2.floodFill*).
- Fitting circles to the binarised image's features via the “Hough circle transform” method to detect circles in an image, including the overlapped ones (*cv2.HoughCircles*).
- Fitting the detected circles to a log-normal distribution to obtain the statistical parameters of average bubble size and deviation.

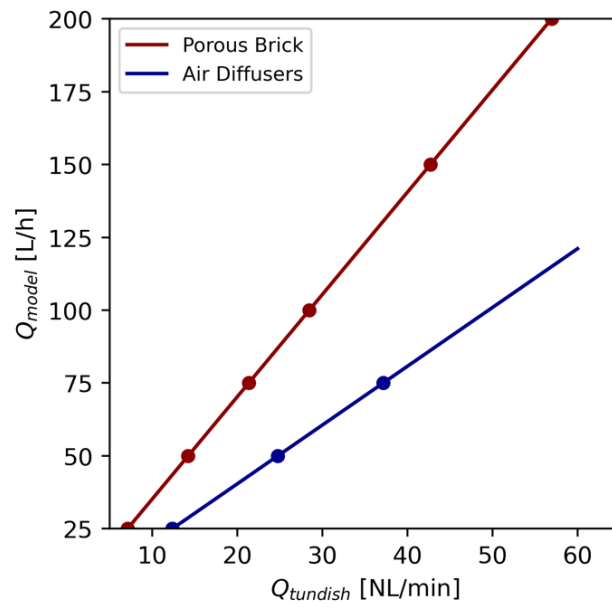


Figure 4.5: Correlation between gas flow rates of industrial tundishes (in NL/min) and the corresponding value in the water model (in L/h) by keeping “ U_g ”.

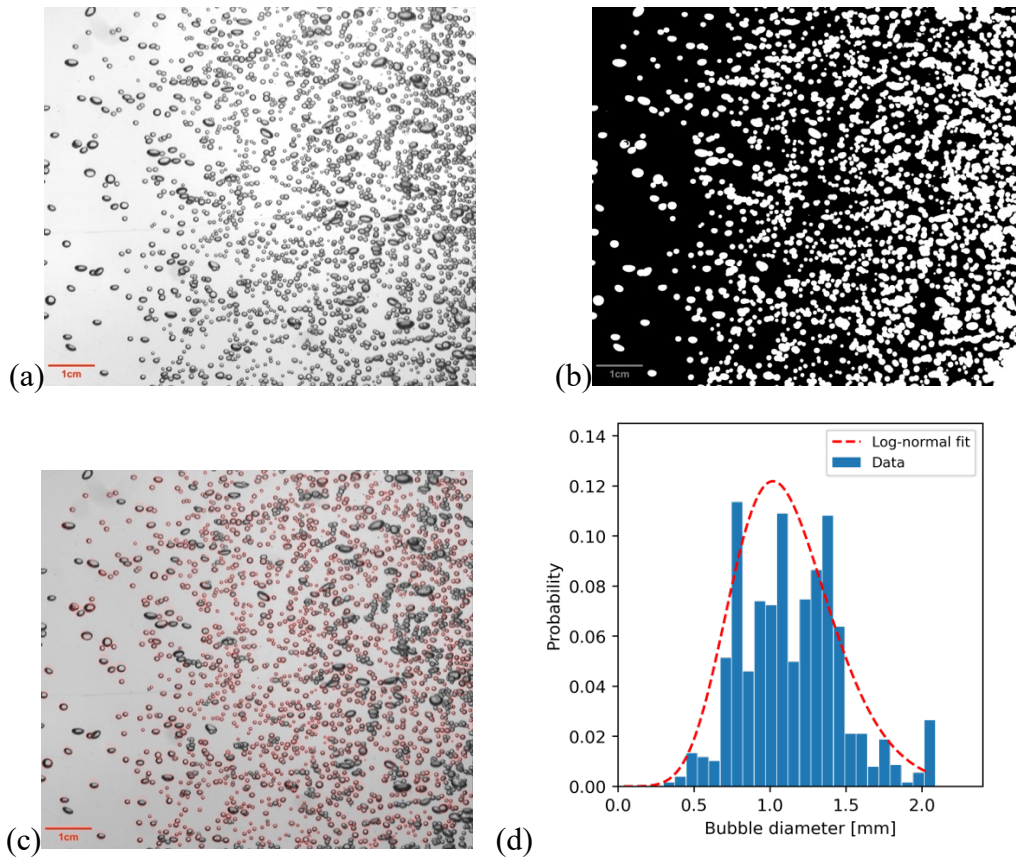


Figure 4.6: Bubble shadowgraphy and image analysis showing (a) the original image, (b) the binary one, (c) the superimposition of detected circles and (d) the fitted curve.

The characterisation of bubble size distribution using the shadowgraphy technique coupled with image analysis is summarised in Figure 4.7, based on the log-normal fits of Figure 4.8, highlighting that the bubble plumes are slightly affected by the gas flow rates. In general, the air diffusers generate an average bubble of 0.6 mm (0.2 - 1.4mm), whereas the porous brick produces 1.1 mm bubbles (0.7 - 1.6mm). Compared to the optimum size range described in the literature (0.5 - 2.0mm), the porous brick generated bubbles within the suggested limits, whereas the air diffusers were closer to the lower limit. According to the literature (95), the smaller bubble size would increase the collision and adhesion probabilities, as well as the detachment one, leading to a lower overall probability of removal. Thus, one might expect a faster pace of particle removal for the porous brick.

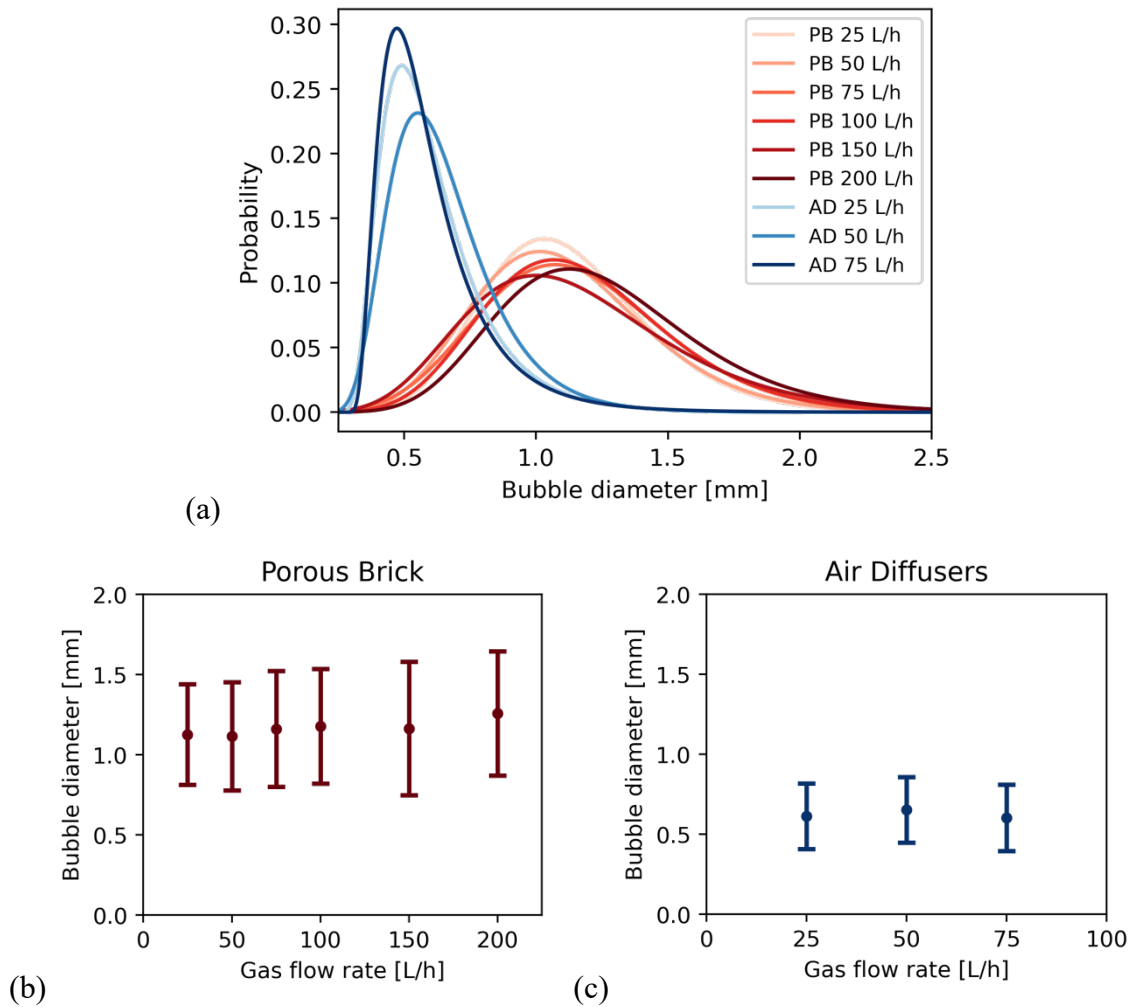


Figure 4.7: (a) Bubble size distribution for the Porous Brick (PB) and Air Diffusers (AD) as a function of the gas flow rate, and (b,c) mean diameter and standard deviation.

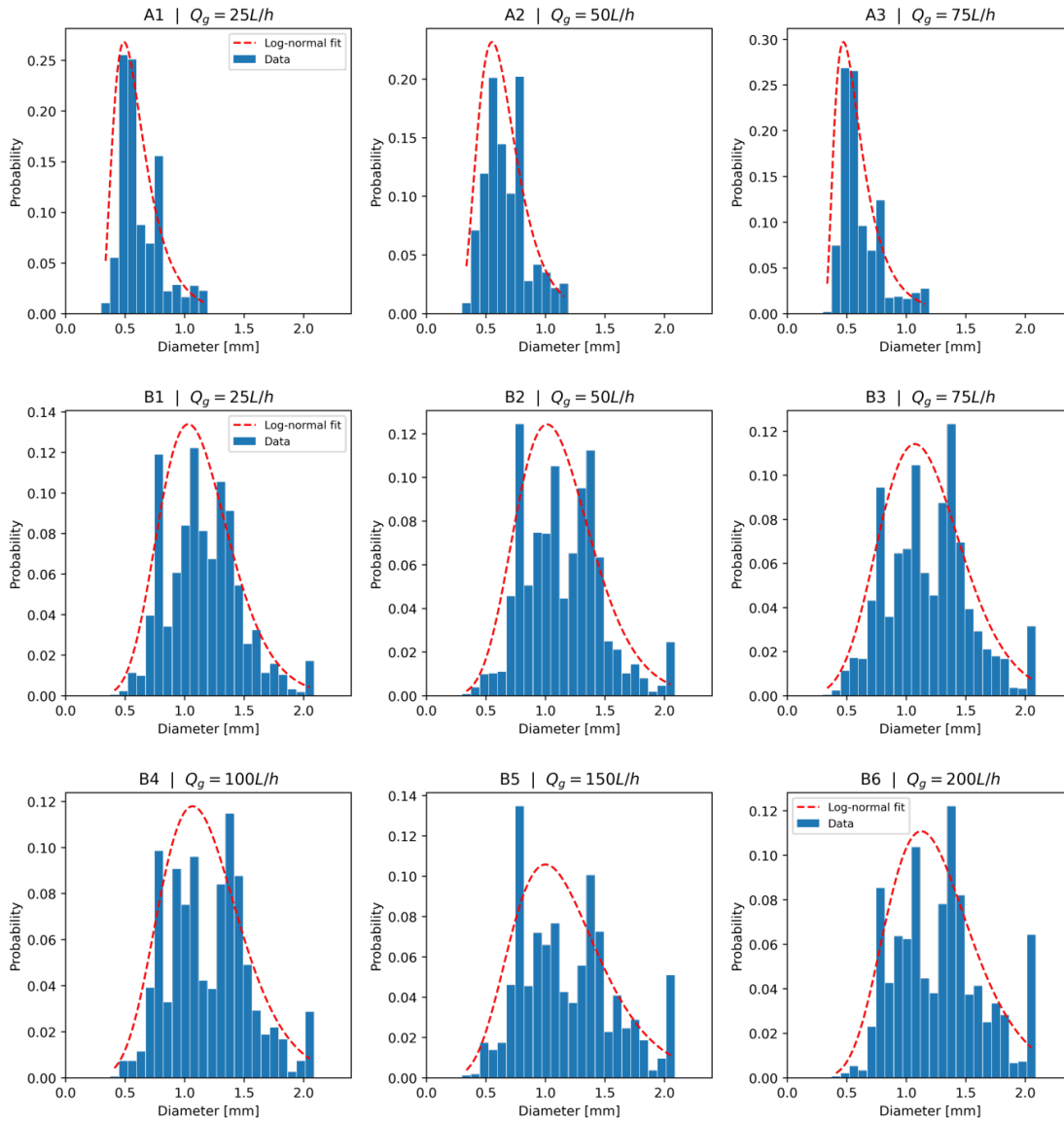


Figure 4.8: Bubble size distributions for the nine conditions of bubble injection considering the air diffusers (A1-3) and the porous bubbler (B1-6).

4.4 Results and discussion

4.4.1 Effect of bubble plume on hydrophobic particle flotation

The particle removal as a function of time for hydrophobic particles was recorded, and the results are presented in Figure 4.9 as a function of the bubbler and the gas flow rate. Considering that the nine experiments began with a natural flotation step, there is a similar pattern in the first 10 minutes after the homogenisation of particles in the system, as no gas is being injected yet. From the moment when the porous structure is blown with

compressed air, some bubbles reach the camera's field of view, scattering light and causing the particle removal to be artificially decreased for a while. These bubbles float right away, and this effect does not disturb the subsequent results, as the bubble plume is already developed. From 10 to 35 minutes, the results represent the combination of natural and induced flotation mechanisms, as bubbles now also help the removal of particles. Comparing the fitted blue curves for the nine conditions, various removal rates and efficiencies are expected.

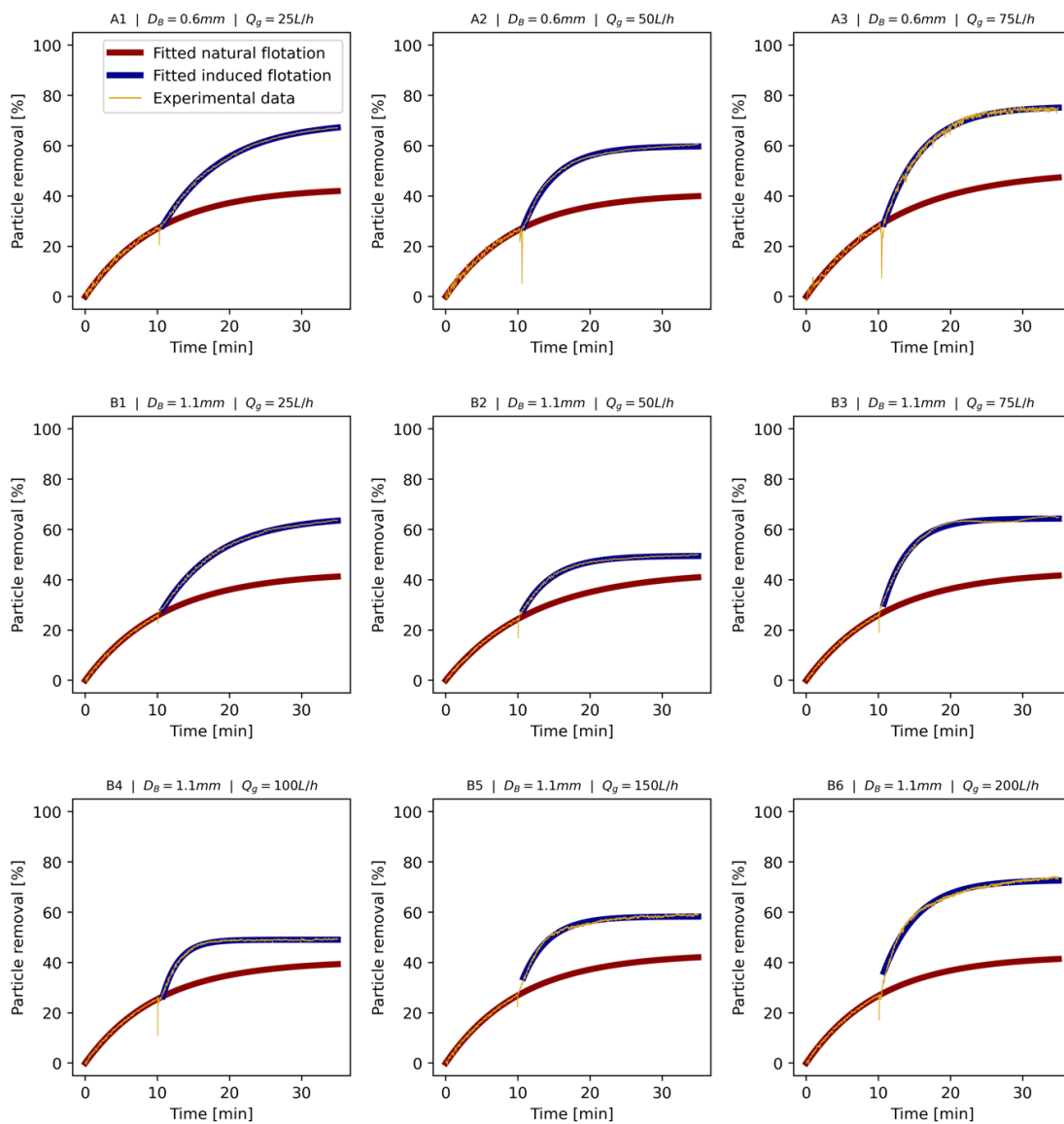


Figure 4.9: Percentage of particle removal as a function of time, presenting the fitted natural flotation (dark red line) and induced one (dark blue line) for the nine combinations of gas flow rate (25, 50, 75, 100, 150, 200 L/h) and bubble size (0.6 and 1.1 mm).

An exponential decay fitting the light intensity data for the natural and induced flotation, and the parameters of time scale and maximum efficiency for each experiment are summarised in Figure 4.10 and Figure 4.11. The average value for the parameters of natural flotation was a time scale of 648 ± 50 s and a maximum efficiency of $43.5 \pm 2.6\%$, with a coefficient of variation of 7.7% and 6.0%, respectively. These values attest to the reproducibility of the experiment's initial conditions (before the bubble plume is injected), providing a direct comparison among the results for induced flotation. Besides, it is worth noticing that although the average efficiency is 43.5%, this value represents an extrapolation at an infinite time, whereas the system has roughly three-quarters of the initial particle concentration still in suspension after the 10 minutes of natural flotation, thus allowing the analysis of the share of induced mechanisms to flotation.

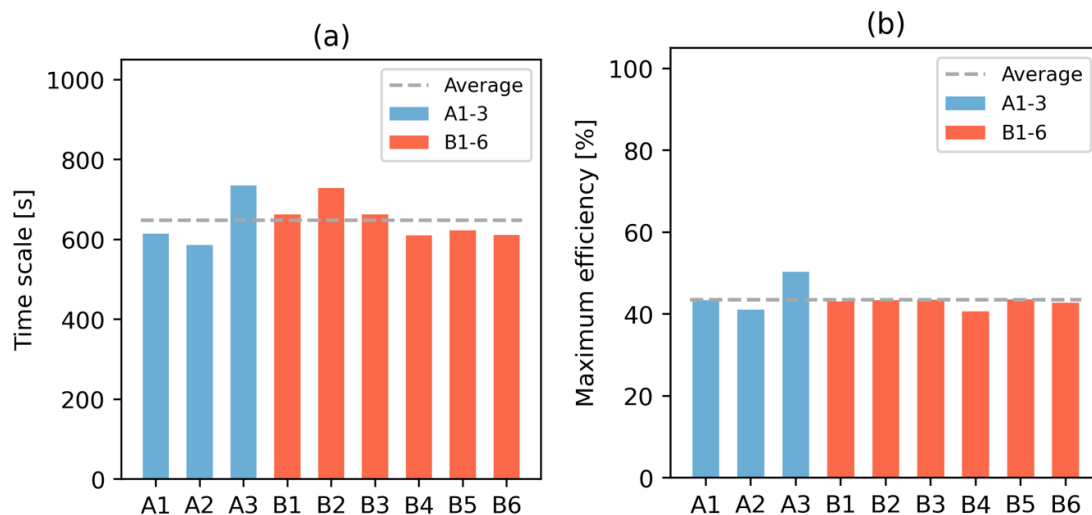


Figure 4.10: The collected (a) time scales and (b) maximum efficiencies for the nine experiments considering only the natural flotation, highlighting the reproducibility of the experiment's initial condition.

To evaluate the performance of the water model in delivering reliable results, one of the experiments was repeated twice (1.1 mm bubbles, 50 L/h gas injection). The obtained flotation parameters were 223 - 257 s for the time scale and 42.4 - 49.6 % for the removal efficiency, leading to a 7.1 % and 7.8 % variation coefficient, respectively. When comparing these values to the ones for plain natural flotation, it is remarkable that

the injection of the bubble plume adds other sources of error to the measurement, increasing mainly the uncertainty for the removal efficiency.

The time scale and maximum efficiency values comprising the share of induced flotation mechanisms are shown in Figure 4.11 and plotted as a function of the gas flow rate per area (U_g). Recalling from the Methods section, the maximum U_g for the air diffusers was 500 L/min/m² (or 75 L/h) because higher gas flow rates would disturb the particle concentration measurement. The averages for the plain natural flotation are also indicated to ease the comparison of values (grey dashed line), highlighting a noticeable decrease in the time scale when the bubble plume is injected, regardless of the bubble size and the gas flow rate. Moreover, the trend seems to be of a U-shaped profile in Figure 4.11a, suggesting an optimal gas flow rate to speed up the particle flotation. The initial decrease in time scale is in tune with other experiments from the literature, where an increase in the gas flow rate caused a higher particle removal rate (i.e., lower TS), even though the authors did not correlate it to a specific flotation mechanism (73,77,76). However, by increasing the gas flow rate even further, the removal rate tends to decrease. The complete behaviour may be analysed considering the three mechanisms of flotation induced by bubbles: (i) surface attachment, (ii) wake capture and (iii) flow-induced removal.

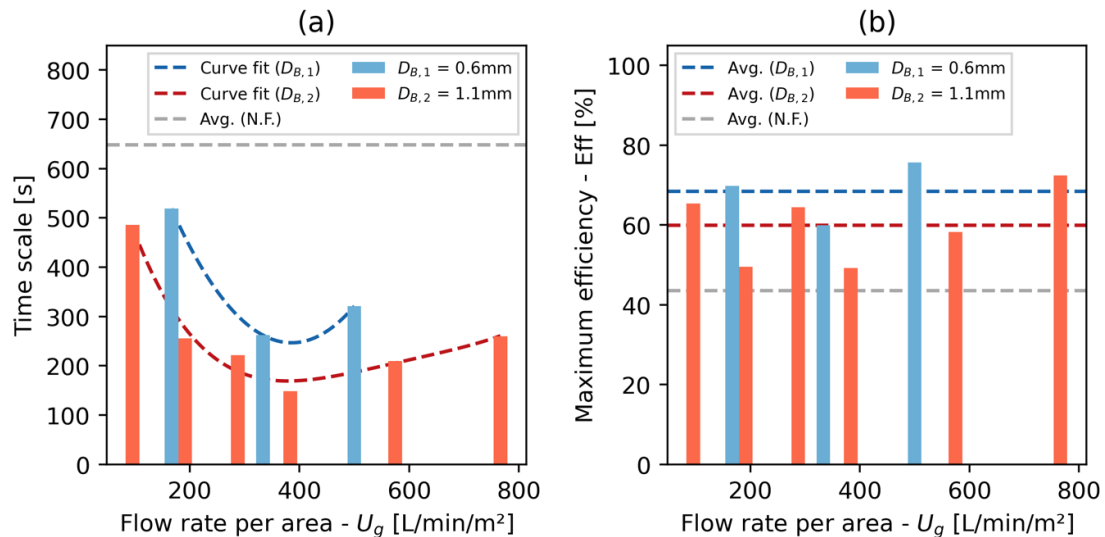


Figure 4.11: The collected (a) time scales and (b) efficiencies for the nine experiments considering both the natural and induced flotation, comparing the results to the average of plain natural flotation (grey dashed lines).

Even though the effect of the gas flow rate on the likelihood of bubble-particle attachment and volume of bubble wake region is typically discussed in the literature for a single bubble, one might expect that their magnitudes are proportional to the number of bubbles in the plume. Thus, as the bubble size was not significantly affected by the gas injection in this report, a higher flow rate should induce mechanisms (i) and (ii) (particle attachment and bubble wake capture, respectively), leading to a proportional increase in the removal rate. However, it is worth comparing the marginal increase of the removal rate when the gas flow rate rises from 95 to 190 L/min/m² (90% faster, for 1.1 mm bubbles) and from 190 to 380 L/min/m² (72% faster), as the latter is less noticeable. This effect is likely because the collision probability and the wake region of an individual bubble are affected by the neighbouring bubbles in the plume, not representing a simple addition of the shares from each one. Besides, when increasing the gas flow rate even further, from 380 to 770 L/min/m² for 1.1 mm bubbles, an increase in the time scale is seen in Figure 4.11a, indicating a lower removal rate. A first hypothesis on the reason behind this effect could be the recirculation pattern induced by the bubble plume, whose velocity scales with the cubic root of the gas flow rate, according to the literature (104). By mass conservation, the velocity of the ascending plume scales with the horizontal flow velocity in the top region of the model, which reduces the time for the floated particle to be transferred to the liquid's free surface. However, the recordings of the bubble plumes at 50Hz during the experiments show that the vertical velocities are similar. In numbers, 291 and 273 mm/s for 50 and 200 L/h, respectively, which are in accordance with the expected rising velocity of 295 mm/s for 1.1mm bubbles (26). Besides, the vertical velocity for the 0.6mm bubble plume was evaluated in 360 mm/s (at 25 L/h), close to the theoretical value of 384 mm/s (26). Consequently, as the bubble size remains the same (Figure 4.7), a higher gas flow rate leads to more bubbles per volume for a constant residence time of the plume in the system. Another hypothesis is that a larger number of bubbles reaching the system's free surface per unit of time causes higher turbulence, disturbing the transfer of the particle to this top layer. If so, it could not be investigated further with the current setup. Overall, although an increase in the gas flow rate is beneficial to the induced mechanisms of flotation (26,15), it might spoil the removal rates at high values.

Regarding the influence of the bubble size on the time scale, a lower overall probability of particle removal would be expected for the plume with smaller bubbles and, thus, longer times for the particle flotation. This behaviour is depicted in the results of Figure 4.11a, where bubbles of 1.1 mm presented a lower time scale when compared to the 0.6 mm ones for U_g below 500 L/min/m². Besides, Yang et al.'s work (15) discusses that larger bubbles have a positive effect on the bubble wake region, mainly for the ones large enough to assume non-spherical shapes (spheroids or spherical caps). Their results show a decrease in the capture rate of the bubble wake zone when bubble diameters decrease from 12 to 2.5 mm. By extrapolation, an increase of 17% in the time scale could be expected when decreasing the bubble size from 1.1 to 0.6 mm. Thus, the lower removal rates for the 0.6mm bubbles could be linked to the lower effectiveness of the mechanisms “i” (particle attachment) and “ii” (bubble wake capture). Nevertheless, the results for maximum efficiency (Figure 4.11b) are not supposed to be affected by these mechanisms, as this parameter is an extrapolation to an infinite time. In other words, lower removal rates will lead to longer times for the flotation to occur, but not to lower efficiencies.

Analysing Figure 4.11b, smaller bubbles (0.6mm) could remove more particles in suspension, leading to higher efficiencies. However, there is no clear trend for this parameter as a function of the gas flow rate. Thus, clustering the results by bubble size (dashed lines), the average efficiency was calculated as $68.4 \pm 6.5\%$ for 0.6 mm bubbles and $59.8 \pm 7.3\%$ for 1.1mm ones. Compared to the average efficiency of natural flotation (44.1%), the bubble plume's share removal of hydrophobic particles is noticeable.

4.4.2 Insights into the industrial practice

The question now raised is, “What can we learn from the results, and how can we apply them to the practice of bubbling in the tundish, removing the maximum number of inclusions?”. The similarities between the water model and an industrial tundish are typically discussed in dimensionless numbers, like the Froude (Fr), Reynolds (Re) and Eötvös (Eo) numbers (105). The Reynolds number (Re) states the ratio between inertial and viscous forces, whereas the Froude number (Fr) is related to the ratio of inertial to gravitational forces, and their similarity assures that bulk flow phenomena are well reproduced in the water model (106). When using water to replicate the liquid steel, the only condition where both Fr and Re similarity conditions are met is having a 1:1 physical

model (70), assuring that the bulk flow phenomena are well reproduced (106). As this report studied the contribution of bubbles to particle flotation, it is also important to have similar Eötvös numbers (E_o), a ratio between gravity and surface forces. Combined with Re , ensure the similarity of bubble shape in the liquid, as introduced by the Grace diagram in Figure 4.12. Even though the relative E_o between water and liquid steel is 3.8 (106), it is worth highlighting that this diagram is built on a log scale, meaning that systems with Re and E_o numbers within the same order of magnitude will have a comparable bubble shape.

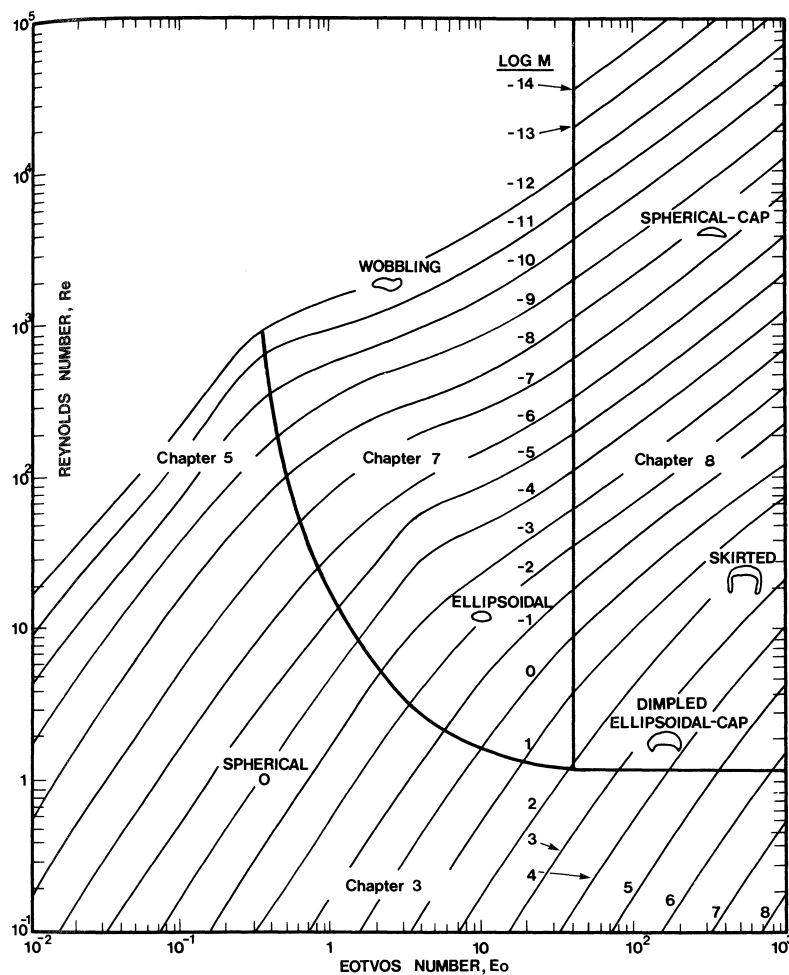


Figure 4.12: Diagram depicting the shapes of bubbles rising in liquids (Grace diagram) (107).

It is worth highlighting that the terminal velocity of the bubble, calculated by the Stokes Law (89), is expected to be close in both liquid media due to the similar kinematic

viscosity between water and molten steel. This means an approximately equal residence time of the bubble plume in ascension and an analogous particle-bubble kinetic energy during collision (17). Naturally, one must account for the effect of gas expansion due to temperature and pressure differences, leading to a 1.3% or 8.3% larger bubble diameter in water or liquid steel (0.4m-high liquid column), respectively - corresponding to 2.7 or 17% faster ascension. For the steel tundish, the effect of temperature could worsen this scenario, increasing the relative expansion to 61%. However, this latter effect can be neglected, considering that 0.6mm bubbles take less than 2 seconds to leave a 0.4m-high tundish, hardly reaching the steel temperature.

Therefore, primary insights can be obtained from water modelling, supporting the industrial practice of bubbling inert gas into the tundish. An additional similarity regarding the bubble plume must be addressed before applying the current results to an industrial tundish. Although the bubble diameter injected in the liquid steel by porous structures is within the 2-20mm range (22,23,105), one might assume that engineered purging devices could generate the same bubble size distributions applied in this report. For this purpose, controlling plug parameters such as the pore diameter and surface wettability could help to achieve smaller bubbles (64).

Compared to the results for plain natural flotation (Figure 4.10), the gas injection decreases the required time for particle flotation (TS) and increases the maximum efficiency that could be attained. Industrially speaking, various parameters can be adjusted while installing a bubble curtain in the tundish, such as the gas flow rate, the bubbler area, and the target bubble size. Starting with the gas flow rate, the results suggest an optimum value for which the time scale would be the lowest, attained at around 300 to 500 L/min/m² for both bubble sizes. This condition could be applied to relatively shallow tundishes (1:1 scale, as previously discussed) and converted to industrial gas flow rates of 20 to 35 NL/min when considering the commercial “purging beam” (Figure 4.5). This range could also be a starting point for other industrial setups, although novel water models would be required to get insights about particular geometries of tundishes.

As there was no clear trend between the maximum efficiency of removal and the gas flow rate, it is important to remember that this value represents an extrapolation at an infinite time. For example, a ladle could attain this condition by increasing the bubbling time as the molten bath recirculates in this vessel. However, the tundish works as a buffer,

and the tools to increase the residence time of the liquid metal in this vessel are limited to flow modifiers (such as dams and weirs). Therefore, it is crucial to have high removal rates (i.e., low time scale) to ensure maximum cleanliness of the liquid metal in a short time. Alternatively, more bubble curtains can be installed in the tundish or a larger area covered by the porous bricks, increasing the interaction time between the liquid metal and the bubble plume while remaining within the optimum range for U_g .

In order to illustrate it, Figure 4.13 presents a calculated scenario for 0.6 and 1.1mm bubbles, comparing their performance as a function of the number of interactions with the bubble plume. Considering that Figure 4.11a defines an optimum value for the gas flow rate close to 385 L/min/m², the expected Time Scales would be 247 and 169 s for 0.6 and 1.1mm bubbles, respectively. Coupled with the mean maximum efficiency from Figure 4.11b, the particle removal across time was determined by the exponential decay function - Equation (3.7). Besides, Figure 3.11b estimates the recirculation time to be close to 50 seconds, which is in tune with the estimated value of 47 seconds, considering the model's volume of 17 L (including 5 L for the tubing) and the recirculation rate of 21.6 L/min (at 30% of the pump power). This period could be correlated to a single pass through a bubble plume in the tundish. Having this information in mind, Figure 4.13 shows that a single pass removes 12.6% of particles when 0.6mm bubbles are applied, while 15.3% are removed when the bubble has a 1.1mm diameter. For a better comparison, these percentages could be normalised by the maximum efficiency of the air diffuser (68.4%), showing that a single pass removes 18.4% and 22.4% of the maximum, respectively. For two passes, these values increase to 22.8% and 26.7% (33.3% and 39.0% of the maximum), respectively, achieving 43.6% and 46.2% (63.7% and 67.5%) after five passes. Interestingly, it takes seven passes for both bubble plumes' performance to be the same, from when the 0.6mm bubbles begin to remove more particles than the 1.1mm ones. Due to the exponential behaviour of particle removal, it takes 5-6 passes for the 1.1mm bubbles to remove 80% of its maximum efficiency (i.e., 47.8% efficiency), but 10 passes to remove 95%.

Summarising, the results for the two bubble plumes (0.6- and 1.1-mm bubbles) define a trade-off between shorter removal times and higher maximum efficiencies (Figure 4.11). For example, the bubble size distribution closer to the lower limit of the optimum range (0.6 mm) presented a higher "TS" and "Eff", meaning that it would take

longer to achieve the efficiency plateau, but more inclusions would be removed. Hence, it might still be attractive to design porous bubblers to generate smaller bubbles, but with the aforementioned considerations to increase the interaction time with the plume. On the other hand, tiny bubbles tend to be trapped in the liquid metal flow, and their use must be carefully considered so as not to generate pores in the solidified steel.

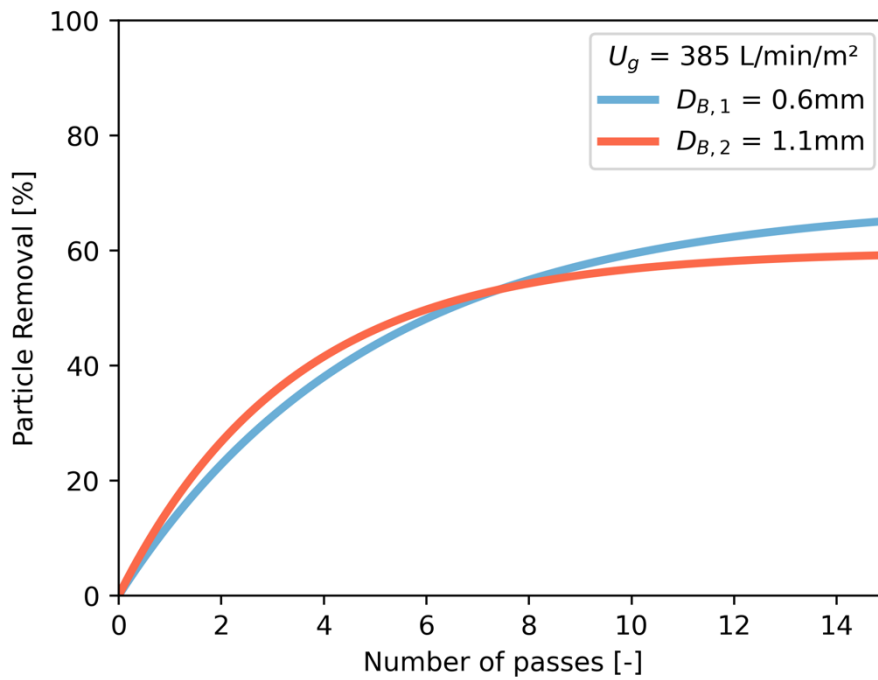


Figure 4.13: Calculated scenario for particle removal at the optimum gas flow rate (385 L/min/m²) as a function of the number of passes through the bubble plume.

Complementarily, one must remember that the current setup of the water model applies a recirculating flow of particle suspension. Thus, the removal rate at the first moments of gas injection better represents the interaction with the bubble plume in the tundish, and higher values would mean a more effective purging device for a given gas flow rate. Following this idea, Equation (4.4) is obtained by taking the derivative of Equation (3.7) and evaluating the removal rate at $t = 0$.

$$\left. \frac{dI}{dt} \right|_{t=0} = -(I_o - I_\infty) \cdot \frac{1}{TS} \quad (4.4)$$

By taking a close look on Equation (4.4) and considering that the light intensity is normalized between 0 and 100% for the flotation experiments, the first term is given as the initial intensity ($I_o = 100\%$) minus the percentage at an infinite time (I_∞), which represents the maximum removal efficiency. In other words, Equation (4.4) is directly proportional to the ratio between Efficiency and Time Scale, allowing Figure 4.14a to be obtained, which compares the various gas flow rates and bubble diameters. From this result, the highest initial removal rate was obtained at 380 L/min/m² for 1.1mm bubbles, and at 500 L/min/m² for 0.6mm bubbles. However, the removal rate at this latter condition is still 29% lower, meaning that fewer particles would be removed at a single pass through the bubble plume.

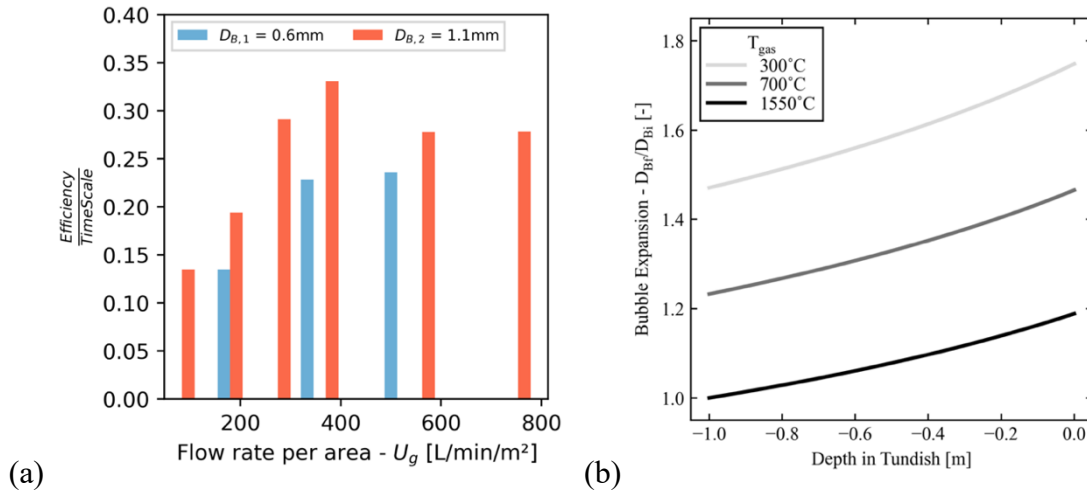


Figure 4.14: (a) The ratio between maximum efficiency and time scale, representing the initial removal rate, for the various conditions of experiments. (b) The ratio of bubble expansion considering liquid steel at 1550°C.

Another way to look at the results is to consider that bubbles expand in the tundish as a function of the ferrostatic pressure. For example, considering a 1m-deep tundish, bubbles expand by 20% from the injection surface to the steel's top layer, as seen in Figure 4.14b. Thus, 0.6mm and 1.1mm bubbles would reach 0.72 and 1.32mm diameters, respectively. Additionally, an additional expansion might be caused by the temperature difference between the liquid steel and the injected gas. In the same example, the bubble would be 47-75% larger when the gas is heated from 300 to 1550°C, reaching up to 1.05

and 1.92mm diameters. Thus, the behaviour of a plume of 0.6mm bubbles could approach the one for 1.1mm bubbles due to gas expansion in the tundish.

4.5 Conclusion

In this chapter, the kinetics of inclusion removal in liquid steel have been investigated by using a tundish-like water model in a quasi-2D configuration. Hollow glass spheres were applied to reproduce the concentration of inclusions, and two distinct porous structures were applied to generate the bubble plume, leading to mean diameters of 0.6 and 1.1mm. Bubble shadowgraphy and image analysis were applied to characterise the bubble's size distribution in the plume, while light scattering allowed the particle concentration to be measured along the experiment. The exponential decay has been fitted and the parameters of "time scale" (TS) and "maximum efficiency" (Eff) determined the flotation performance and were considered to analyse the variables in this study: mean bubble size, gas flow rate and particle wettability.

Analysing the flotation experiments for hydrophobic particles and variable gas injection, the results indicated an optimum gas flow rate for which the time scale was the lowest, leading to faster removal rates. This behaviour of a U-shaped curve was correlated to the mechanisms of bubble-induced flotation. On the other hand, as the maximum efficiency represents an extrapolation of the exponential decay at an infinite time, there was no clear trend of this parameter as a function of the gas flow rate. In summary, this value increased from 43.5% for the plain natural flotation to 68.4% and 59.8% for 0.6- and 1.1-mm bubbles, respectively. On the other hand, the smaller bubbles led to a higher time scale (slower removal rate). Therefore, a trade-off between removing more inclusions and attaining this condition in a shorter time is defined by the bubble size.

Applying these results to the industrial practice in the tundish, the project of a porous brick should consider the number of bubble curtains and the bubbler's coverage area, as longer interaction times with the bubble plume might be required to attain high efficiencies. For instance, although smaller bubbles (0.6mm) led to a higher maximum efficiency, it would take more than 15 passes through the bubble plume for this value to be attained, which seems unfeasible in an industrial tundish. On the other hand, the 1.1mm bubbles displayed a lower time scale, translating into short times to reach the maximum removal efficiency. For this latter bubble plume, the efficiencies at the optimum gas flow

rate (385 L/min/m^2) were estimated for one, two and five passes in 15.3%, 26.7% and 46.2%. In other words, 80% of the removable particles are floated after 5-6 passes, while 10 passes are required to reach 95%. Thus, the tundish shows great potential to increase the steel's cleanliness, but it should work together with the porous plug in the ladle to attain low concentrations of inclusions.

CHAPTER 5 – COUPLING THERMODYNAMIC CALCULATIONS AND PREDICTIVE MACHINE LEARNING MODELS TO ESTIMATE SLAG FOAMING PERFORMANCE

5.1 Introduction

Another role of bubbles in steelmaking is to promote foaming of the slag layer, a phenomenon that improves energy efficiency but can also lead to operational disruptions. Thus, controlling foam stability is of utmost importance and relies on the chemical composition of the slag, which directly dictates its physical properties. This Chapter introduces the topic of slag foaming by developing a framework to estimate the viscosity, surface tension and density of slags, coupling a commercial computational thermodynamics-based solution with an open-source machine learning model pre-trained on glasses and ceramic melts. Its performance is compared to experimental data for steelmaking slags. After validation, the potential of this framework is explored with some examples.

5.2 Literature review

Concerning steelmaking slags, the old saying “Look after the slag and the metal will look after itself” has never been more relevant in steelmaking, particularly when pursuing low-sulphur, impurity-free and clean steel grades (108). Given the high temperatures at which oxide slags operate (above 1400°C), it is reasonable to expect their phases to be close to the thermodynamic equilibrium, as kinetic mechanisms will not limit reactions from occurring (109). In this scenario, the chemical composition of slag is determinant for its phase distribution (liquid fraction and precipitates) and physical properties, such as viscosity, surface tension, density, electrical and thermal conductivity (110). Considering the different roles of slags in steelmaking, a parallel may be drawn between their properties and performance, for instance:

- i. The control of impurities in liquid steel includes the removal of sulphur in the primary metallurgy. Together with high sulphur partitions, lower viscosities (μ) are desirable to enhance desulfurization capacity when the slag is in contact with liquid steel (111).

- ii. Although bubble-induced flotation is vital to remove non-metallic inclusions from steel, this goal is only accomplished by transferring them to the slag phase. This process ensures that inclusions will be dissolved and not return to the molten bath. Yet, the ease of transfer depends on low interfacial tensions (γ) between liquids (slag and metal) (112).
- iii. Moreover, metallurgical slags must also support industrial practices. For example, the slag density (ρ) directly affects the formation of the so-called “slag eye”, dictating the exposed area of the liquid steel to the surroundings. Thus, a trade-off is sought between a larger area to allow the injection of ferroalloys and a limited exposure to the atmosphere, which leads to the formation of non-metallic inclusions (113).

While individual properties may be related to different roles of the slag, sometimes a single phenomenon may rely on multiple properties, as in the case of slag foaming, which depends on the viscosity, surface tension and density, concomitantly (114). Although this phenomenon is widely discussed for the primary metallurgy of steels in the Electric Arc Furnace (EAF), which will be further discussed in Chapter 6, the foaming of the slag may also be observed in other reactors:

- In the Blast Oxygen Furnace (BOF), an emulsion of slag, gas and metal is generated to promote the refining of the liquid steel, increasing the surface area for interfacial reactions to occur (115);
- During vacuum build-up in the Vacuum Degasser (VD), the low pressure inside the reactor induces the formation of bubbles in the molten metal and intensifies their expansion as they rise to the slag layer. Depending on the bubble stability in the slag, it may create a layer of foam, causing operational disruptions (116);
- Even in the Ladle Furnace (LF), a foamy slag can be expected. For instance, using calcium carbide (CaC_2) as a deoxidiser generates CO bubbles as a product, causing a transitory foaming of the slag, depending on the conditions (117).

In order to investigate the easiness of generating and sustaining the slag foaming, Ito and Fruehan (118) have introduced a parameter named foaming index (Σ), representing the ratio between the height of the sustained foam (h) and the superficial gas

velocity - calculated as the gas flowrate (Q) per unit area of the cross-section (A), as in Equation (5.1). Later, many works have sought correlations with the physical properties of the slag, as presented in Equations (5.2) to (5.7) - note that some equations were derived for specific systems, i.e., acidic, basic, or MgO-saturated slags (118,119,120).

$$\Sigma = \frac{h_{foam}}{\frac{Q_{gas}}{A_{section}}} \quad (5.1)$$

$$\Sigma = 570 \frac{\mu}{\sqrt{\gamma \rho}} \quad (5.2)$$

$$\Sigma = \begin{cases} 115 \frac{\mu}{\sqrt{\gamma \rho}} & \text{(basic)} \\ 0.93 \frac{\mu}{\gamma \rho^{2/3}} & \text{(acidic)} \end{cases} \quad (5.3)$$

$$\Sigma = \begin{cases} 115 \frac{\mu^{1.2}}{\gamma^{0.2} \rho D_B^{0.9}} & \text{(basic)} \\ 10.3 \times 10^4 \frac{\gamma^{12}}{\mu^{0.4} \rho^{11.7} D_B^{23}} & \text{(acidic)} \end{cases} \quad (5.4)$$

$$\Sigma = 10^6 \frac{\mu E_{eff}}{(\rho g)^2 D_B^3} \quad (5.5)$$

$$\Sigma = 100 \frac{\mu^{0.54}}{\gamma^{0.15} \rho^{0.39}} \quad (5.6)$$

$$\Sigma = \begin{cases} 214 \frac{\mu}{\sqrt{\gamma \rho}} & \text{(basic)} \\ 999 \frac{\mu}{\sqrt{\gamma \rho}} & \text{(MgO sat.)} \end{cases} \quad (5.7)$$

As these equations were empirically fitted to better describe a slag system under study, various coefficients and exponents were obtained. Even so, general trends can be deduced from this set of equations: the viscosity (μ) seems to directly influence the foaming index, whereas the surface tension (γ) and the density (ρ) are inversely correlated. The only exception is for Equation (5.4), in which Σ is directly proportional

to γ and inversely to μ for acidic slags. To improve visualisation, Equations (5.2) to (5.7) are plotted against each other in Figure 5.1, assuming unit values for the bubble diameter (D_B) and the effective elasticity (E_{eff}). The comparison emphasises how the different coefficients and exponents change the sensitivity of the equations to each of the slag's properties. More specifically, it highlights that further clarification is required on how to estimate foamy slag stability, as the calculated foaming index values vary across studies.

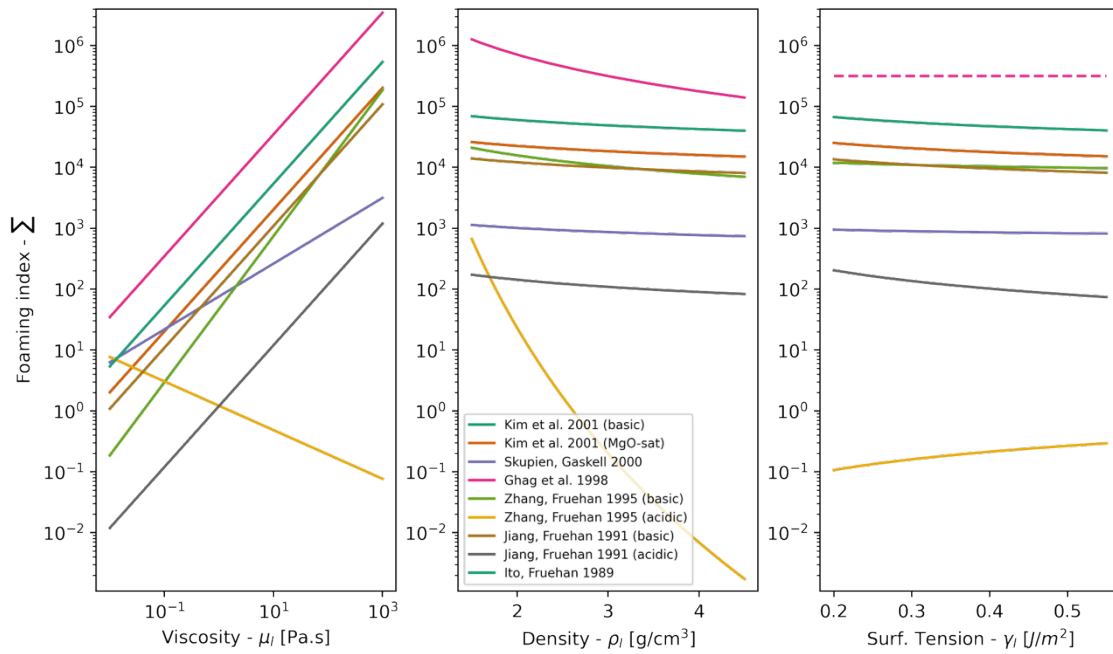


Figure 5.1: Calculated foaming indexes (Σ) for typical values of viscosity, density and surface tension - based on Equations (5.2) to (5.7) and assuming D_B and E_{eff} equal to the unit.

As highlighted by Conejo (7), the fundamentals of foaming in aqueous systems might also be applied to better understand the phenomena involving slag foaming and the ageing mechanisms that act to collapse the foam layer. Modelling it consists of defining the specific times associated with the period for each mechanism to occur (121):

- i. Coarsening (t_{cs}) by the transportation of gas from smaller to larger bubbles;
- ii. Drainage (t_{dn}) of the liquid film in bubble walls, and;
- iii. Coalescence (t_{cl}) of neighbour bubbles (or rupture to the atmosphere) as the liquid film becomes too thin.

The specific times for each mechanism to occur might be calculated from equations in the literature, as presented in Equations (5.8) to (5.10). However, their value relies on complex variables that are not available to slag systems at high temperatures, which can be categorised into (122,123,121):

- Gas-dependent parameters: gas diffusivity (D_f), Henry constant (He), ideal gas molar volume (V_m); gas density (ρ_g) in $\Delta\rho_{lg}$;
- Geometrical parameters: bubble radius (R_B), area covered by thin film (f), geometrical constant (B), foam height (H), volume fraction (Φ), permeability constant (K);
- Constants to be determined (and their typical values): C (0.37–5.202), p (0.75–4.5), q (0.6–0.84), r (0.75–1.5), s (0.25–0.46) and α (0.5–1.0).

$$t_{cs} = \frac{R_B^2}{D_f \text{ He } \gamma_{lg} V_m f B} \quad (5.8)$$

$$t_{dn} = \frac{H \mu_l}{K \rho_l g R_B^2 \Phi^\alpha} \quad (5.9)$$

$$t_{cl} = C \cdot \frac{\mu_l R_B^p (\Delta\rho_{lg} g)^q}{\gamma_{lg}^r A_{BB}^s} \quad (5.10)$$

Thus, an alternative approach is to isolate the variables of interest in Equations (5.8) to (5.10) by assuming that gas-dependent and geometrical parameters do not vary with slag phase, and to account for their fractional change, as exemplified in Equation (5.11). This approach cancels out the parameters assumed constant and others (as “C” and “g”), leaving the fractional change as a function of the viscosity (μ_l), density (ρ_l) and surface tension (γ_{lg}), as well as the modified Hamaker constant (A_{BB}). Regarding this later parameter, the literature presents experimental evidence that A_{BB} is directly proportional to the surface tension (124) and its influence will be assumed as already computed in t_{cl} .

$$Qt_n = \frac{t_{n,2}}{t_{n,1}} \quad (5.11)$$

This approach leads to the time ratios in Equations (5.12) to (5.14), as a function of changes in slag's properties ($Q\mu_l$, $Q\rho_l$, $Q\gamma_{lg}$). The subscripts “cs”, “dn” and “cl” denote the mechanisms of coarsening, drainage and coalescence, respectively, and the powers “s” and “r” are constants in the range of 0.60-0.84 and 0.75-1.50, respectively. It is essential to note that an increase in Qt_n indicates a longer time for the ageing mechanism to occur and collapse the foam, which correlates with a higher foaming index (Σ). Also, generally speaking, the time ratios are directly proportional to the viscosity and inversely proportional to the density and surface tension, as discussed in Equations (5.2) to (5.7) - the exception being Qt_{cl} , which is directly proportional to ρ_l .

$$Qt_{cs} \approx \frac{1}{Q\gamma_{lg}} \quad (5.12)$$

$$Qt_{dn} \approx \frac{Q\mu_l}{Q\rho_l} \quad (5.13)$$

$$Qt_{cl} \approx \frac{Q\mu_l \cdot Q\rho_l^q}{Q\gamma_{lg}^r} \quad (5.14)$$

The challenge of estimating these properties and, consequently, the slag performance based on its chemical composition has driven the development of empirical models to fit experimental results (110). In parallel, large databases on glasses and molten ceramics have become available, and machine learning methods have been applied to predict the properties of glass based on its chemical composition. One example is the GlassNet model, which is based on the SciGlass database and is available as a Python library (125). Although the model is primarily developed for glasses, the database also contains information on molten ceramics, enabling the slag properties to be estimated and evaluated. Besides, Muire et al. (126) discuss the lack of available databases for slag compositions and properties, as the current ones are still the 2nd edition of the Slag Atlas (1995) and a handbook by Prof. Ken Mills (2011), restricting the training of machine learning models specifically to slag systems.

In this chapter, experimental compositions of typical metallurgical slags and slag conditioners were investigated using the GlassNet model. The estimated values of

viscosity, surface tension and density were compared to experimental measurements from the literature. To illustrate the applicability of this framework to select potential conditioners for foamy slags, the addition of Na_2O to an EAF slag was investigated, and the change in specific ageing times was calculated.

5.3 Methodology

To define the scope of this work, the following species were considered for steelmaking slags: Al_2O_3 , CaO , FeO , Fe_2O_3 , MgO , MnO and SiO_2 . Additionally, to extend this analysis to slag conditioners, the following compounds were also added: CaF_2 , K_2O , Na_2O , P_2O_5 , and TiO_2 . Thus, these 12 oxides and fluorides comprise our subsystem of interest.

5.3.1 GlassNet model

The neural network model was developed by training it on 218,000 glass compositions from the SciGlass database, enabling the prediction of 85 properties (125). Figure 5.2 shows the resulting statistical distribution when filtering the compositions made up by the 12 species listed above, yielding 31,006 experimental entries. As the database was built for glasses, the compositions with a high concentration of SiO_2 are remarkable, with a median content of 55 wt%. Additionally, it provides extensive data for CaO -containing glasses at concentrations lower than 25 wt%, whereas Al_2O_3 and MgO ones have numerous data points below 10 and 5 wt%, respectively, and $\text{FeO}/\text{Fe}_2\text{O}_3$ is limited to diluted concentrations. The model is also trained on pure substances (100 wt%), although focused on glass compositions where multi-component systems are targeted. Therefore, given the discrepancies in the chemical composition of steelmaking slags, it becomes vital to validate the model's forecasts before employing it to investigate slag foaming conditioners.

The model also predicts the temperature dependence of specific properties, although some restrictions can be observed. For the viscosity, the temperature is included during model training, allowing this property to be predicted as a function of this variable. On the other hand, the density and surface tension can be forecasted for discrete temperatures, with the highest value at 1673 K (1400 °C). The consequences of this limitation on GlassNet predictions for slag systems are discussed in the following results.

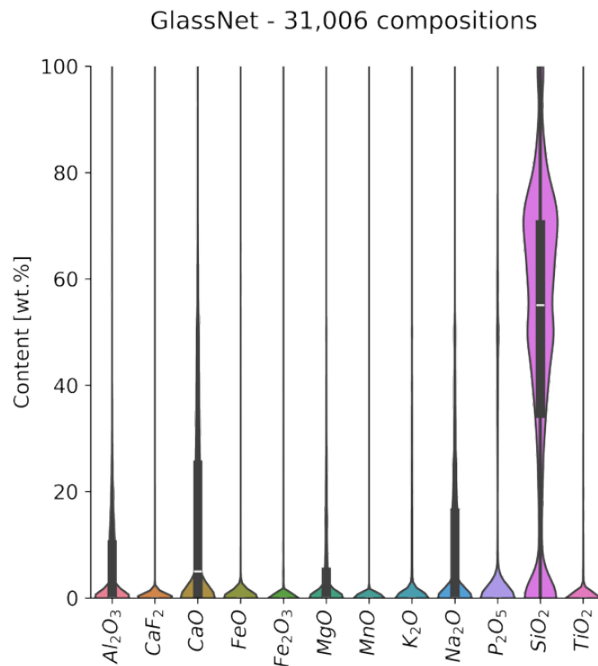


Figure 5.2: Statistical distribution based on SciGlass entries considering the 12 species of interest in this work.

5.3.2 Experimental data

To compare the performance of the GlassNet model in predicting slag properties, experimental data from the literature were considered. Thus, the Slag Atlas (110) presents a comprehensive dataset of viscosity, surface tension and density values, as well as chemical, thermal and optical properties. In numbers, Slag Atlas features 26 tables on viscosity data and six others on both surface tension and density. Additionally, it presents 100 figures with viscosities for binaries, ternaries, or high-order systems, 140 figures with surface tensions and 100 figures with densities. However, it is worth highlighting that these slags are not the same for the datasets of the three properties and, thus, their statistical distributions of chemical composition are analysed for the viscosity, surface tension and density - Figure 5.3a, Figure 5.5a and Figure 5.6a, respectively.

Considering the 12 chemical species of interest, 522 viscosities, 202 surface tensions and 92 density values were extracted from the tables and figures of the Slag Atlas. Although the reference is limited to data obtained before 1995 (2nd edition), the authors' choice was based on the reliability of the reference in revising the methods by which the data were obtained and compiling them into binaries, ternaries and higher-order

diagrams. For example, the viscosity data from the Slag Atlas are primarily obtained from calibrated methods for both room-temperature and high-temperature materials.

5.3.3 Viscosity data from FactSage

It is known that FactSage 8.3 (127), a commercial solution based on the Calphad method, also includes a module to estimate slag viscosity based on its oxides and fluorides, as well as the temperature. The implemented model considers the pair fractions following a quasichemical model and an Arrhenius-like equation to estimate this property based on the slag composition and temperature, respectively (128). Although the method is robust and well-validated for industrial slags, limitations on the available oxide and fluoride components become a drawback. To illustrate this, for example, when considering Cr- and P-containing slags, Cr_2O_3 and P_2O_5 are not available reactants in this module.

5.4 Results and discussion

5.4.1 Performance of GlassNet in predicting slag properties

Considering that the Slag Atlas is based on industrial slags and not intended to explore the entire range of chemical compositions, an analysis of the statistical distribution of their components was conducted for every set of extracted data. For entries on slag viscosity, the distribution is shown in Figure 5.3a, highlighting Al_2O_3 , CaO , MgO and SiO_2 as the primary components of the slag (typical compositions in the steelmaking), with the remaining oxides and fluorides accounting for less than 10% of them. The next step involves creating a correlation plot between the experimental data from Slag Atlas and the predicted values obtained using GlassNet, as shown in Figure 5.3b.

In general, the predicted viscosities in Figure 5.3b are higher than the measured values. Figure 5.3c corroborates this trend as the statistical distribution of errors between the predicted and experimental viscosities is 1.4 orders of magnitude higher. A likely reason for this discrepancy is that the model is primarily trained on data from glasses, which contain high silica contents (see Figure 5.2), where the silica network tends to increase their viscosity. Considering slags with binary basicity ($B_2 = \text{CaO}/\text{SiO}_2$) higher than 1.0, i.e., a CaO content higher than the SiO_2 , the lime acts as a glass modifier,

reducing the number of bridging oxygens in the silica network and leading to lower viscosities. Therefore, although GlassNet allows a temperature-dependent viscosity to be predicted for a broad composition (including Cr and P), its application to metallurgical slags is restricted by its performance. For the sake of comparison, the same 522 compositions were tested in FactSage 8.3 viscosity models, assuming the unavailable components (as Cr_2O_3 and P_2O_5) equal to zero. The correlation is illustrated in Figure 5.4, where a significant performance improvement is evident. Comparing both models, FactSage predictions achieved an R-squared value of 0.9702, whereas GlassNet yielded only 0.1780.

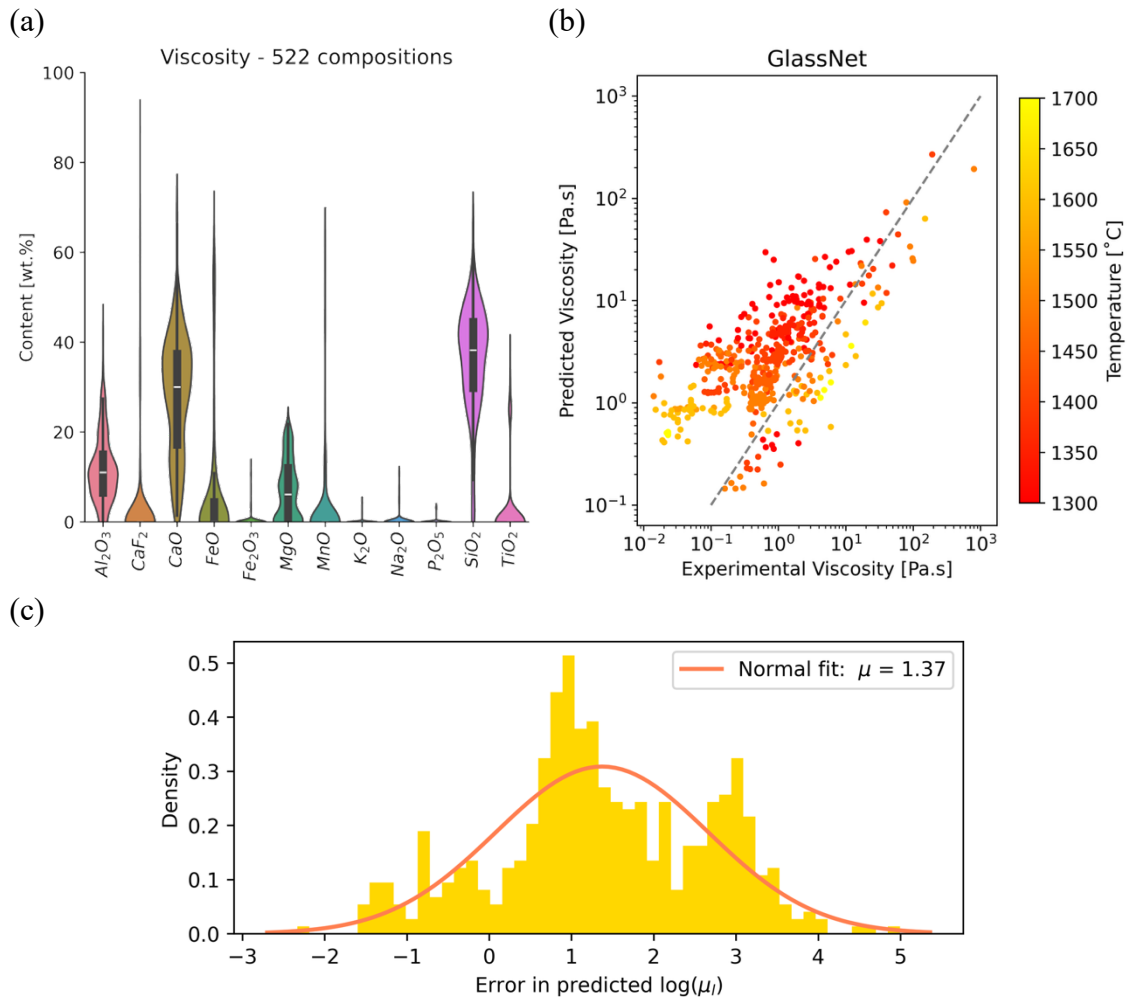


Figure 5.3: (a) Statistical distribution of experimental viscosities from Slag Atlas, (b) its correlation with GlassNet predictions and (c) the statistical distribution of errors.

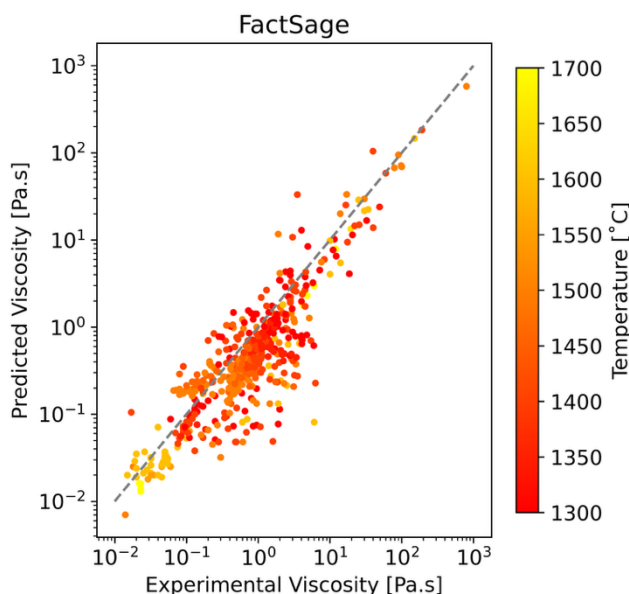


Figure 5.4: Correlation between experimental viscosities from Slag Atlas and FactSage 8.3 predictions, disregarding the content of Cr_2O_3 and P_2O_5 .

The same framework was applied to the surface tension data. Firstly, the statistical distribution of their chemical composition, as shown in Figure 5.5a, indicates that fluorite (CaF_2) is also a major component in the SciGlass dataset, likely due to its well-known surfactant properties. Furthermore, slags have a lower content of SiO_2 , mostly below 30%. Considering that GlassNet was designed for glasses, it is expected that not-so-good correlations would be observed. The results for surface tension are presented in Figure 5.5b, and the predicted values are mostly lower than the experimental ones, as confirmed by the distribution of errors in Figure 5.5c, centred at -0.08 J/m^2 .

Additionally, it is worth remembering that GlassNet predictions are limited to a fixed temperature and data above or below 1400°C are poorly predicted. This effect becomes evident for data points in the upper-right corner of Figure 5.5b, which are horizontally aligned because they had the same chemical composition, and the only variable was temperature. In general, the correlation achieved an R-squared value of 0.6838.

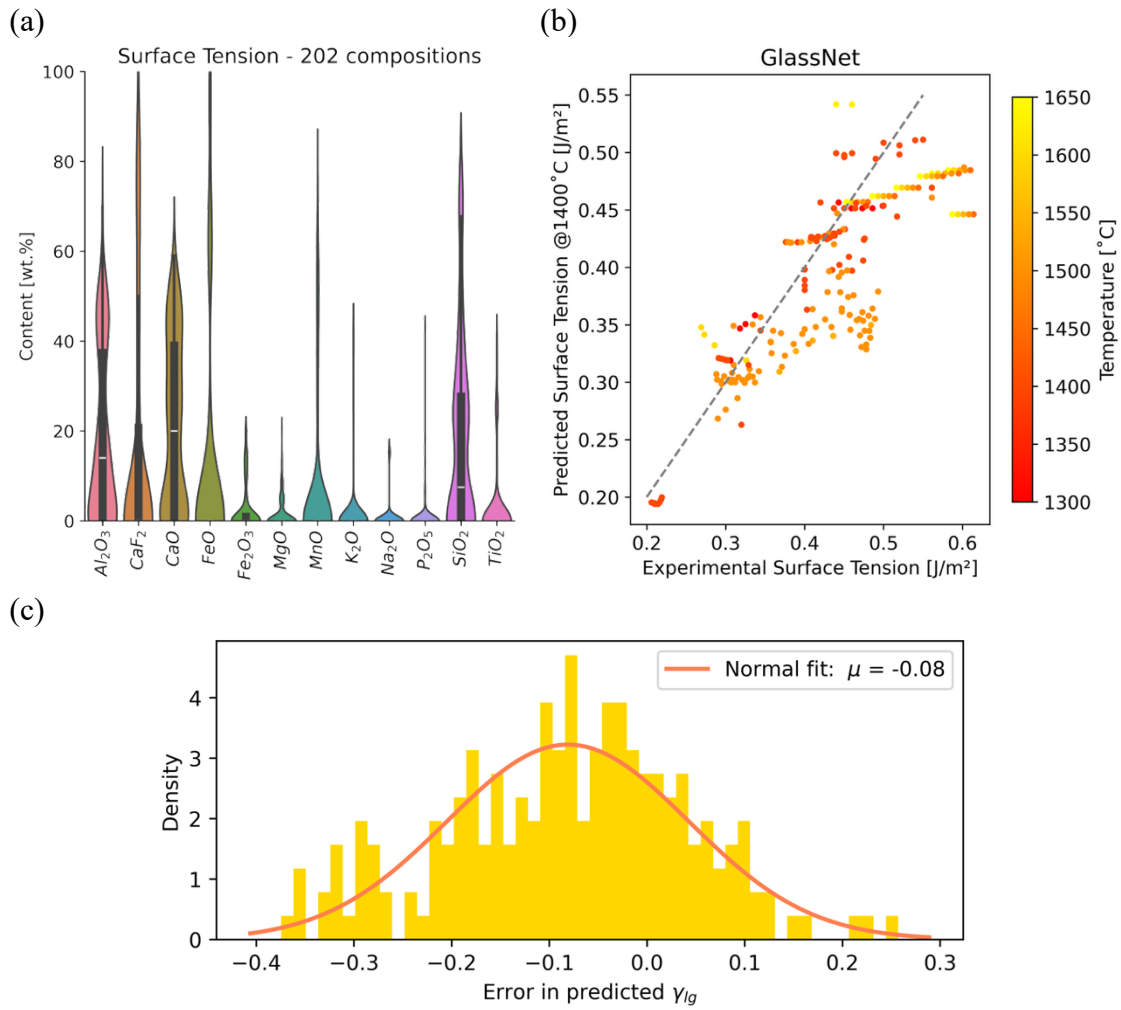


Figure 5.5: (a) Statistical distribution of experimental surface tensions from Slag Atlas, (b) its correlation with GlassNet predictions and (c) the statistical distribution of errors.

The other slag property of interest to be analysed was the slag density, and its statistical distribution of composition is presented in Figure 5.6a. In general, the slags in this dataset are high in CaO , SiO_2 , Al_2O_3 , and FeO , with a notable difference from others (viscosity and surface tension) as they contain data for FeO contents above 20 wt%, closer to EAF's slag compositions. Evaluating the correlation data in Figure 5.6b, the GlassNet model presents a suitable performance for predicting the density of industrial slags, yielding an R-squared value of 0.8134. Also, the statistical distribution in Figure 5.6c shows that errors in prediction are centred at 0.01 g/cm^3 . Once more, the predictions are not temperature-dependent, as it is evident from the results in the lower left corner (at 1600 °C), where they deviate from the ideal correlation ($x = y$).

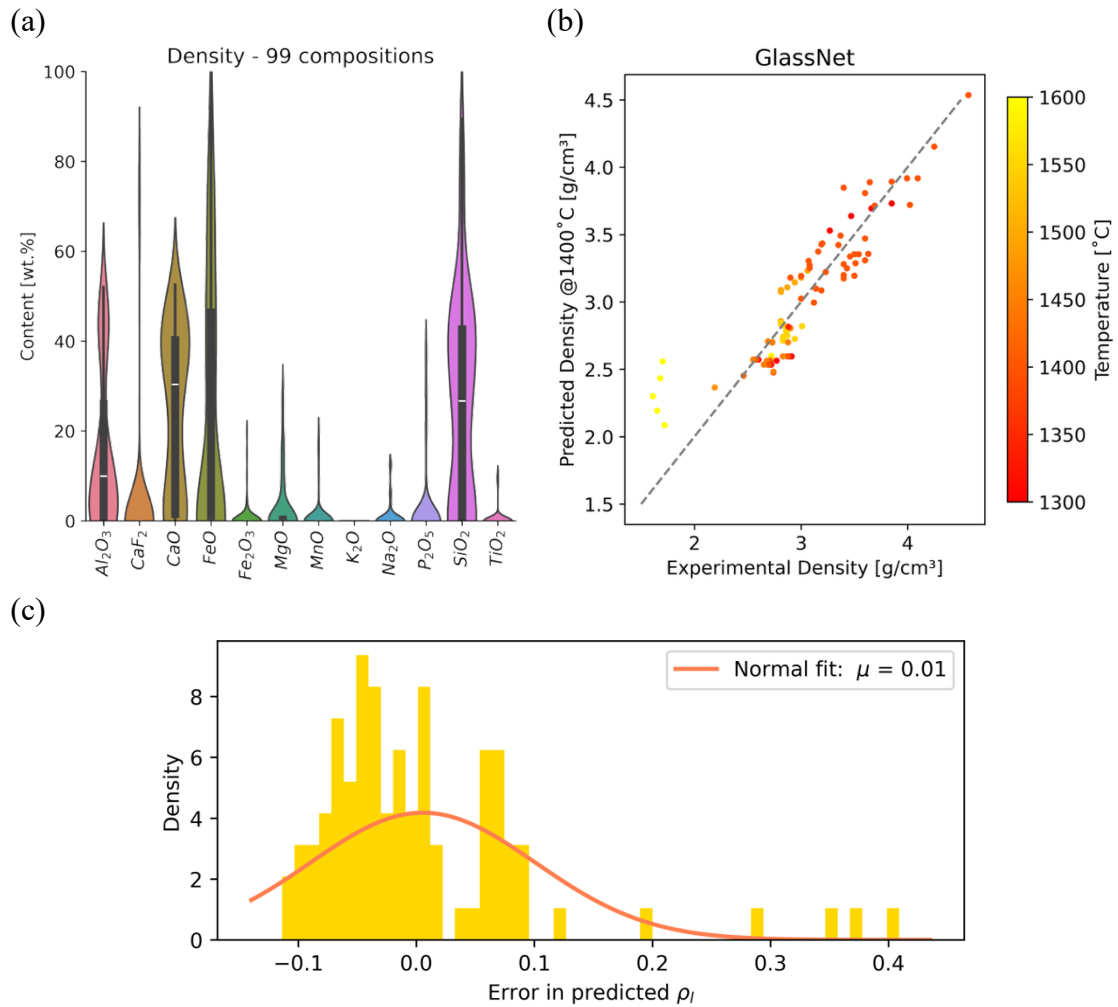


Figure 5.6: (a) Statistical distribution of experimental densities from Slag Atlas, (b) its correlation with GlassNet predictions and (c) the statistical distribution of errors.

5.4.2 Building diagrams of properties based on GlassNet

After investigating the performance of GlassNet to estimate the properties of slag, it is worth highlighting the potential of this tool to calculate ternary diagrams of these properties, a valuable tool for steelmaking. For instance, Figure 5.7 presents the surface tension for slags in the $CaO-SiO_2-MgO$ system, where MgO acts to increase this property. However, it is important to remember that this prediction is at $1400^\circ C$, as limited by GlassNet; i.e., the absolute values should only be considered within the fully liquid region (black solid line, plotted with FactSage 8.3). Outside this region, the results should be taken as a trend, especially for slags at higher temperatures. Another example is presented in Figure 5.8, where four potential slag conditioners are compared by their change in the

surface tension of a $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag. In this scenario, Na_2O seems to be a good candidate as a surfactant, whereas TiO_2 acts to increase this property.

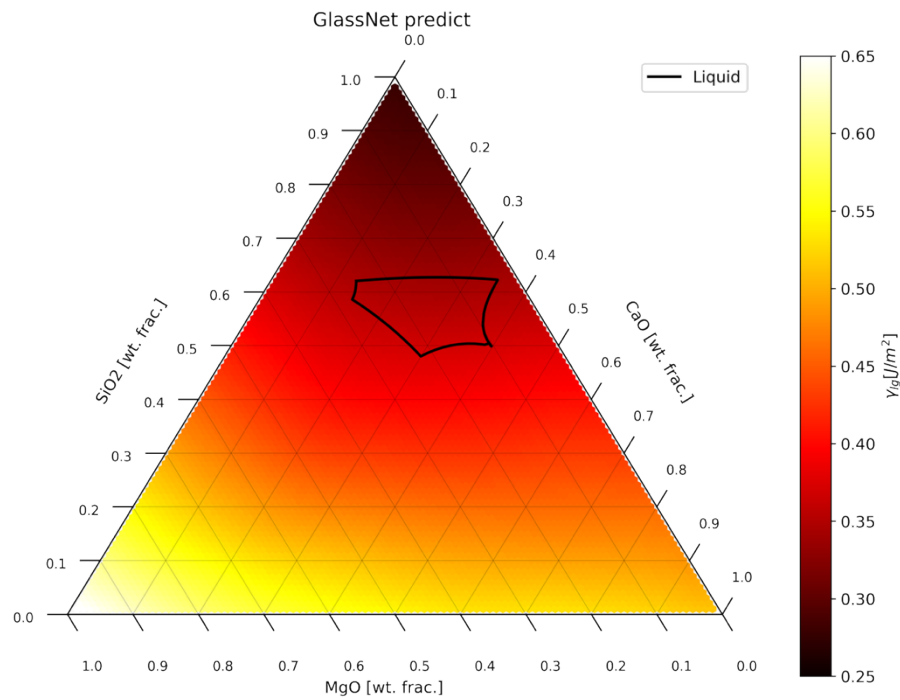


Figure 5.7: Ternary diagram in the CaO-MgO-SiO_2 slag system for the surface tension.

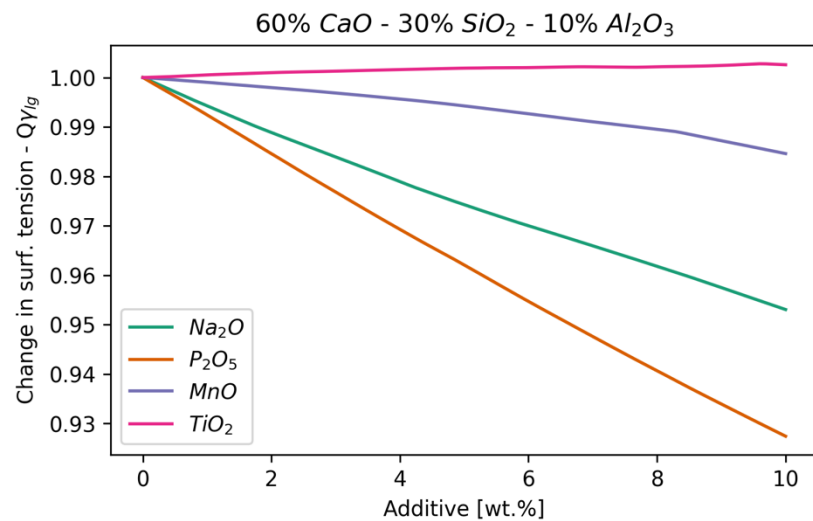


Figure 5.8: Predicted change surface tensions for a CSA slag (fully liquid at 1400°C).

5.4.3 Coupling computational thermodynamics

The performance of the GlassNet model in predicting properties from industrial slags is summarised in Table 5.1. Nevertheless, it is worth noting that such properties are estimated for completely liquid slags, as the experimental dataset had fully liquid compositions. In practice, the solid fraction must be taken into account. The effective viscosity (μ_{eff}) of the slag's global composition can be obtained by Equation (5.15), the Einstein-Roscoe equation (129), considering the viscosity of the slag's liquid fraction (μ_{liq}) and its solid fraction in volume (f) - where the geometrical factor (n) of 2.5 is taken for nearly spherical particles and an interaction factor (α), assumed to be equal to the unit represents a diluted suspension. As the surface tension considers the liquid-gas interface, solids do not directly affect this property's value. Yet, the presence of partially wettable solid particles may act to stabilise the interface by a three-phase contact, which can slow down the foam ageing mechanisms of coalescence and coarsening (130,131,17). The density, in turn, is affected by the presence of solids, but it also requires knowledge of the liquid composition to be estimated. Therefore, coupling the equilibrium calculations from FactSage with the predictive models of GlassNet appears to be a reasonable tool to forecast the foamability performance of the slag.

Table 5.1: Collected R-squared values for the properties' correlations.

Property	GlassNet	FactSage
Viscosity	0.1780	0.9702*
Surface Tension	0.6838	**
Density	0.8134	**

*Disregarding the content of Cr_2O_3 and P_2O_5 in the slags

**Estimation module not available

$$\mu_{eff} = \mu_{liq}(1 - \alpha f)^{-n} \quad (5.15)$$

To illustrate how this procedure supports the selection of slag conditioners to increase foamability, a typical EAF slag was considered, with an initial composition of 15.0 wt% MgO , 6.0 wt% FeO , and a balance of CaO/SiO_2 , according to a binary basicity of 1.5 (132). As the foaming of EAF slag changes the FeO content through oxygen

injection in the molten bath, the range from 6.0 to 35 wt% will be considered for the calculations (x-axis in Figure 5.9 and Figure 5.10), thereby diluting the other species in the slag. Regarding the foam conditioner, although the literature points out the established benefits of P_2O_5 (133), likely due to a decrease in surface tension and an increase in viscosity (134), the viscosity module of FactSage cannot predict P-containing slags. Thus, the injection of Na_2O was studied as an alternative slag conditioner to promote slag foaming. Whereas this oxide is known to reduce viscosity, its role as a surface-active compound might compensate for this effect (57), and the time ratios of Equations (5.12) to (5.14) can simulate it.

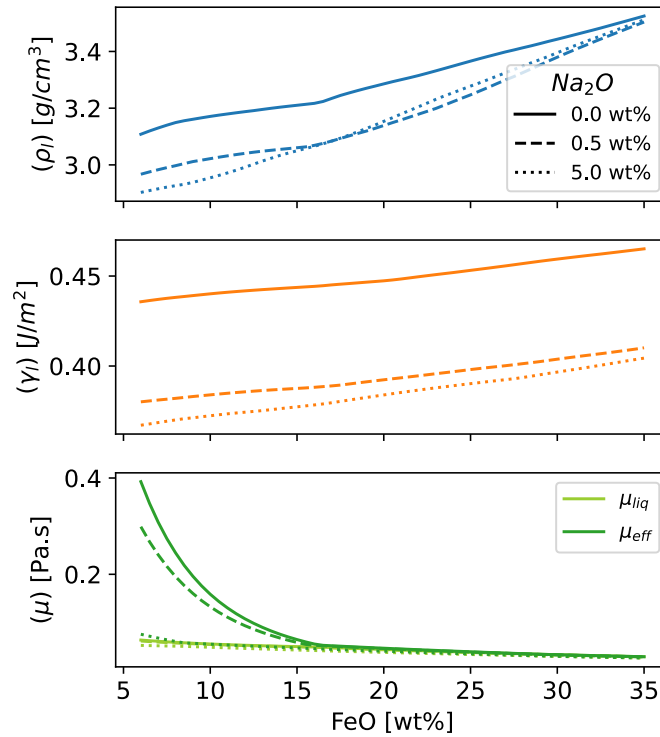


Figure 5.9: The effect of FeO and Na_2O in (a) slag properties of density, surface tension and viscosity.

In Figure 5.9, the estimated parameters are presented for 0.0, 0.5 and 5.0 wt% of Na_2O , investigating the role of Na_2O as a surfactant to decrease γ_{lg} even in low concentrations (0.5 wt%), despite the FeO content. For the density and viscosity, sodium acts to reduce both the density and effective viscosity, calculated by Equation (5.15). For this latter parameter, it is also interesting to note that 0.5 wt% of Na_2O decreased the

effective viscosity by 23.8% whereas the surface tension was reduced by 12.8%. In comparison, 5.0 wt% of Na_2O reduced these parameters by 80.8% and 15.7%, respectively. This steep drop in μ_{eff} (for 5.0 wt% Na_2O) is not only due to the decrease in the viscosity of the slag liquid fraction by 17.5%, but also to the shrinkage of the solid fractions by 37.4%.

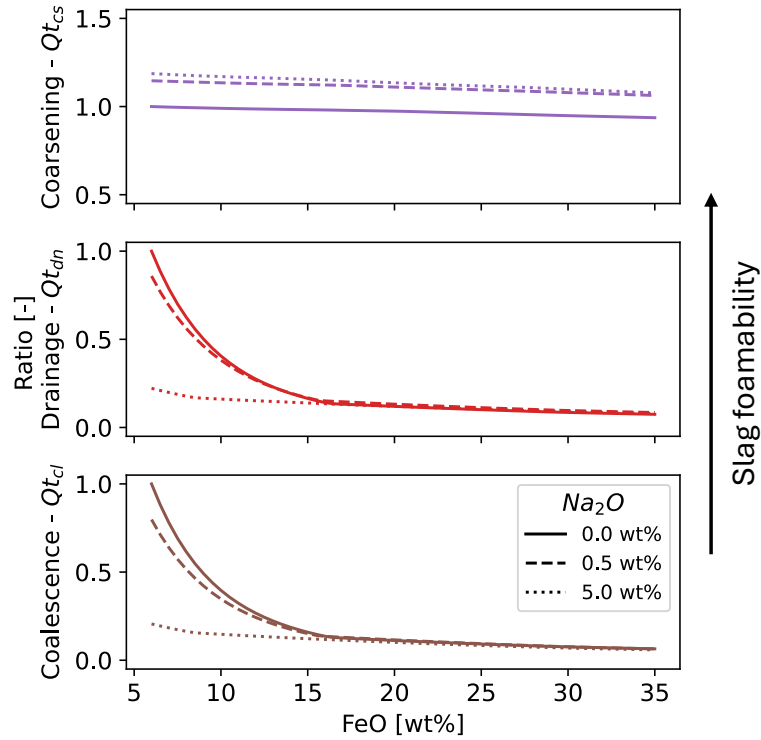


Figure 5.10: The effect of FeO and Na_2O in the ratio of specific ageing times, for a typical EAF slag composition.

However, these parameters alone are not sufficient to predict the stability of a foamy slag, as Equations (5.12) to (5.14) point toward a combined effect of them in dictating the ageing mechanisms of coarsening, drainage and coalescence. Thus, Figure 5.10 presents the time ratios (Qt_{cs} , Qt_{dn} and Qt_{cl}) calculated by the equations above and normalised by the parameters for the slag base composition (6.0 wt% of FeO and without Na_2O), considering $s = 0.72$ and $r = 1.125$. Given the shape of the curves for the drainage and coalescence mechanisms, it becomes clear that slag viscosity plays an essential role in reducing t_{dn} and t_{cl} , thus decreasing the foamy slag stability as the content of FeO increases. Additionally, the loss of stability due to Fe oxidation is more significant than

that caused by the injection of 0.5 wt% Na_2O , indicating a minor downside to this conditioner. In contrast, the injection of 5.0 wt% of the same additive causes a severe decrease in t_{dn} and t_{cl} , even more so for low concentrations of FeO , meaning that it could negatively affect the onset of slag foaming in the EAF. Together with this fact, sodium addition as a surfactant increases the specific time for coarsening, which is sustained during slag foaming (higher FeO contents). This example demonstrates how coupling computational thermodynamics calculations with machine learning predictions supports the investigation of slag conditioners to control foaming, opening an avenue for other alternative compositions to be explored.

5.5 Conclusion

The performance of GlassNet was investigated - a neural network model that predicts the properties of glasses, trained on the SciGlass database, to estimate the features of interest for the slag foamability:

- Viscosity: The predicted values were generally higher than the measured ones, and the R-squared value of 0.1780 reflected this poor correlation. As a benchmark, the FactSage viscosity module displayed a value of 0.9702, although this does not include Cr- and P-containing slags, for example.
- Surface tension: Unlike viscosity, the GlassNet model predictions are limited to an upper temperature of 1400°C, yielding an R-squared value of 0.6838, with estimated surface tension values that are generally lower than the experimental ones.
- Density: As with surface tension, this property was taken at 1400°C. However, a better correlation was achieved, with an R-squared value of 0.8134.

Furthermore, as the composition of the slag's liquid fraction is required to estimate its properties, a coupled framework for obtaining phase equilibria from Calphad-based solutions (and viscosity) and estimating physical properties with GlassNet seems promising. By applying it, an EAF slag composition was investigated, considering Na_2O as a slag conditioner. According to the calculations, 0.5 wt% Na_2O appears to be a promising solution for controlling the coarsening mechanism of foam ageing. Although it negatively contributes to the other mechanisms (i.e., drainage and coalescence), its effect is negligible when compared to the decrease in the effective viscosity of the slag due to the increase in FeO throughout the EAF operation. Overall, this example

demonstrated how this coupled framework could support the investigation of potential foaming slag conditioners in the EAF practice, very likely narrowing down the required number of lab and pilot trials.

CHAPTER 6 – INVESTIGATING ALTERNATIVE SLAG CONDITIONERS TO PROMOTE THE DEFOAMING OF EAF SLAGS

6.1 Introduction

Having developed a framework to investigate the foamability of the slag based on the specific times for the ageing mechanisms to occur, this Chapter focuses on the electric arc furnace (EAF) and the defoaming of the slag as it is tapped to landfilling. A case study is presented in which the current defoaming agent is based on fluorine, which has occupational issues associated with it. Thus, the goal was to identify alternative slag conditioners to add to the slag ladle with a similar capacity to collapse the foamy slag. In this sense, silica sand, sodalite and steel scale were investigated in terms of their effect on the slag's foamability. As this latter presented promising results, a co-product of the steelmaking plant was further characterised and proposed as an alternative defoaming agent for testing.

6.2 Literature review

In the steelmaking process, slag foaming may be observed in various operations, playing an essential role in the electric arc furnace (EAF). In primary metallurgy, the practice of slag foaming is associated with several benefits, such as (7):

- Reduced wear of the refractory lining;
- Acoustic insulation of the electric arc;
- Reduced time for melting the metallic charge;
- Higher energy efficiency with lower electrode consumption.

Figure 6.1 illustrates the effect of the foaming slag layer on the energy efficiency of the electric arc in the EAF. Considering the operation with an exposed long arc (c), the energy transport efficiency to the bath would be expected to be around 36%, with the remainder of the energy being radiated onto the cooled panels and refractories of the electric furnace lining, increasing their wear rate. By foaming the slag, this efficiency reaches typical values of 65 to 93%, given that the coverage of the electric arc by the foam causes the radiation to heat the slag, transferring the thermal energy to the molten bath (7).

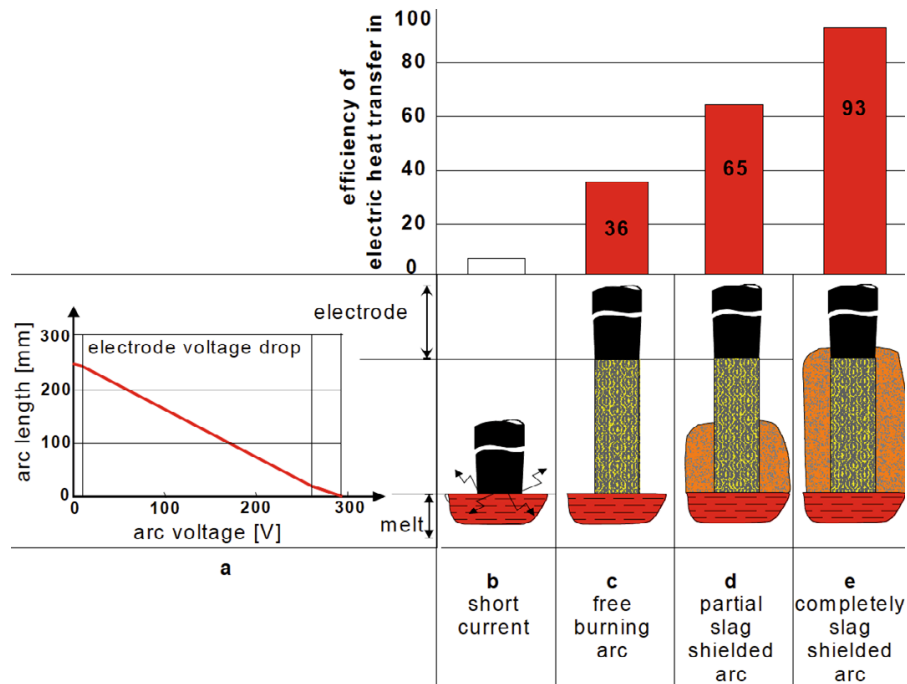


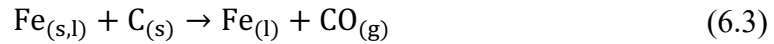
Figure 6.1: Schematic diagram of the influence of the foaming slag layer on the EAF's energy efficiency (7).

Slag foaming in the EAF occurs through the combined injection of a gaseous phase and carbon particles, and can be described in three stages (135,136):

- i. The first step consists of injecting oxygen into the metallic bath with the objective of forming CO bubbles through the reaction with the carbon dissolved in the liquid pig iron - Equation (6.1). Concomitantly, the oxidation of iron also occurs, increasing the FeO content in the slag - Equation (6.2);



- ii. Next, the injection of carbon in the form of coke is carried out directly into the slag, promoting the reduction of FeO and the generation of more CO bubbles - Equation (6.3);



- iii. Then, oxygen is injected directly into the slag to react with the residual carbon, generating further CO bubbles - Equation (6.4).



Thus, it is possible to note that slag foaming in the EAF involves a constant injection of oxygen and carbon, aiming at the formation of CO bubbles. Because this process also causes the oxidation of Fe in the metallic bath, increasing the concentration of FeO in the EAF slag, it is interesting to analyse its phase composition. This can be done using the Isothermal Solubility Diagram (ISD) presented in Figure 6.2, which expresses the variation of FeO on the x-axis, MgO on the y-axis, and the remaining mass balance follows a CaO/SiO₂ ratio of 1.5 — also called binary basicity (B₂) (132).

Considering a starting FeO of 6 wt.%, the arrows indicate the evolution of the slag composition as a function of Fe oxidation and the consequent dilution of the other slag components. For example, although the green line (12 wt.% MgO) and blue line (14 wt.% MgO) start from the same phase composition, the former becomes completely liquid starting at 16 wt.% FeO, whereas the latter would require more than 30% FeO to enter the completely liquid field. Thus, the composition following the blue line remains saturated in MgO for a longer time, lessening the chemical corrosion of the refractory lining and presenting a precipitated second solid phase.

To evaluate the capacity of a slag to retain such foaming, the foaming index (Σ) is typically used, according to Equation (5.1). Additionally, the stability of the foamed slag can be evaluated by its lifespan, considering the ageing mechanisms already presented in Chapter 5: coarsening, drainage, and coalescence/rupture. In this sense, studies indicate more stable foamed slags in the face of ageing mechanisms through the increase of the solid fraction and, consequently, the effective viscosity (137) - Figure 6.3.

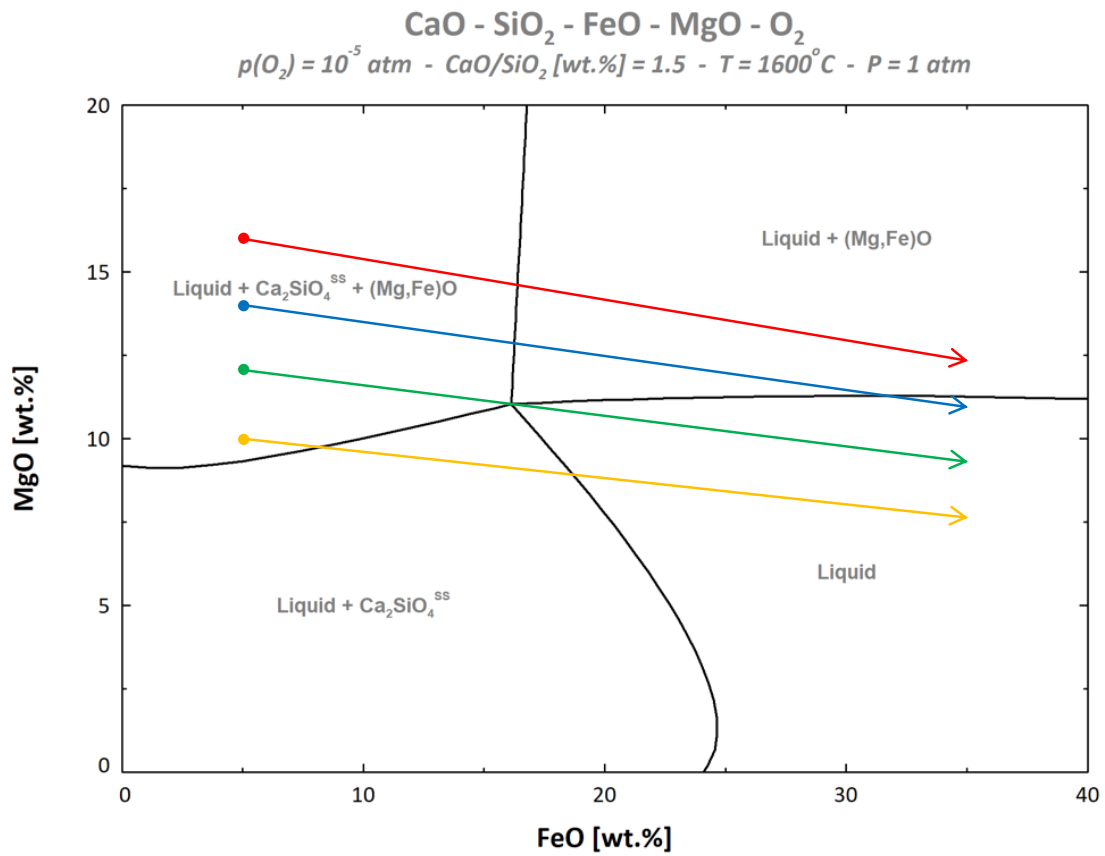


Figure 6.2: ISD of an EAF slag, showing the influence of the initial MgO content. Adapted from (132).

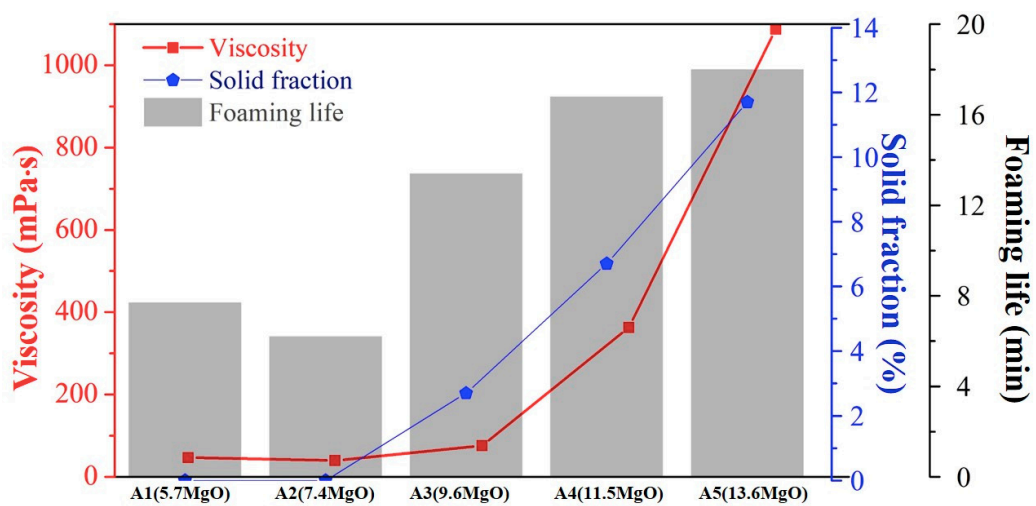


Figure 6.3: Effect of MgO content on viscosity, solid fraction, and foam lifespan for an EAF slag composition (137).

Although the main challenge for foaming slags in the EAF involves adjusting the chemical composition of this phase to allow the onset and upholding of foaming during furnace operation, some steelworks face a collateral problem. Depending on the EAF design, foaming slag overflow during and at the end of refining may be directed to slag pots (or slag ladles), whose volume must be dimensioned considering that the slag will arrive still expanded by the presence of gas bubbles. However, if the slag pot presents a limitation such that it cannot support the rate of excess slag generation, a process of killing the foamed slag becomes essential. That is, accelerating the ageing mechanisms to collapse the generated foam and reduce the volume required for its transport to the disposal yard. From this point of view, the development of a "defoaming agent" involves the inverse logic of slag stabilisation in the EAF, adjusting its chemical composition to accelerate foam ageing mechanisms.

In this sense, modelling slag foamability based on its chemical composition allows adjustments to be made to the process, resulting in foaming during refining in the EAF and collapsing the foam during disposal. Allied to this, two recent trends in steelmaking can be cited that reinforce the importance of predicting the effect of slag chemical composition on its foamability:

- With the search for iron ore reduction processes with a lower carbon footprint, the incorporation of DRI (Direct Reduced Iron) and HBI (Hot Briquetted Iron) into the electric furnace charge brings with it impurities such as Al_2O_3 , K_2O , TiO_2 (138);
- The investigation of possible uses for less pure fractions of recycled refractories (for example, the layer closest to the working face) as slag conditioners may bring contaminations of Cr_2O_3 , Al_2O_3 e MnO (139).

Therefore, the present chapter evaluates the effect of different additives on the stability of foaming slag, based on the change in characteristic times associated with the foam ageing mechanisms ($Q_{t_{cs}}$, $Q_{t_{dn}}$, $Q_{t_{cl}}$), indicative of the slag foamability. A commercial briquetted product for application in the slag pot was evaluated, characterising its chemical and mineralogical composition. Based on the results obtained, the method developed in Chapter 5 was applied to predict the characteristic times and investigate the mechanism of action of such a commercial solution. Subsequently, silica

sand, sodalite, and steel scale were studied as alternative additives, with the latter raw material being selected for experimental characterisations and in-depth investigations, indicating its potential benefit for collapsing foaming slags between the electric arc furnace and the slag pot.

6.3 Methodology

6.3.1 Slag composition under study

The base slag considered for this study has its chemical composition presented in Table 6.1, originating from the electric arc furnace. In an initial analysis, it is noted that the slag is mainly composed of CaO, FeO, SiO₂ e MgO, and that the other components are present in contents equal to or less than 5 wt.% on average. Regarding the binary basicity (B₂) of this slag, considering the CaO/SiO₂ ratio, a value of 3.5 ± 0.3 is reached. Furthermore, the component with the greatest variation amplitude is FeO (6.9 wt.%), probably due to sampling throughout the primary refining process.

Table 6.1: Composition of the slag under study over seven measurements. Results provided by the partner company.

wt. %	FeO	Al ₂ O ₃	CaO	MgO	MnO	P ₂ O ₅	S	SiO ₂	TiO ₂
#1	22.9	3.18	44.4	10.65	4.78	0.89	0.06	12.79	0.42
#2	23.1	3.17	44.1	10.81	4.71	0.91	0.07	12.72	0.42
#3	29.8	2.69	37.5	9.72	5.81	1.08	0.05	12.90	0.47
#4	25.2	2.47	42.3	10.38	5.00	1.08	0.05	13.14	0.42
#5	26.0	2.36	43.0	10.34	4.93	0.96	0.05	12.02	0.39
#6	26.6	2.17	43.0	11.06	5.00	0.87	0.06	10.87	0.37
#7	27.6	2.65	42.0	10.09	4.88	0.84	0.06	11.47	0.40
$\bar{x}$	25.9	2.7	42.3	10.4	5.0	1.0	0.057	12.3	0.42
σ	2.5	0.4	2.3	0.4	0.4	0.1	0.006	0.8	0.03

To evaluate the effect of possible defoaming conditioners on this base slag composition, the method established in Chapter 5 will be applied, considering the computational thermodynamics software FactSage 8.3 (GTT-Technologies, Germany) for phase equilibrium and viscosity estimation, and GlassPy (v. 0.4.6) - a library in Python which encompasses the GlassNet model for predicting surface tension and density. The chemical composition of the considered additives is presented in Table 6.2: silica sand,

sodalite, and steel scale. Other additives were investigated for their effects, but are not presented in the results due to their negligible contribution to slag defoaming: blast furnace slag, cryolite, sodium hydroxide, cooking salt, and carbon.

Table 6.2: Chemical composition by weight considered for possible defoaming slag conditioners (140,141,142).

[wt.%]	Silica sand	Sodalite	Steel scale
SiO₂	95.2 - 99.1	56.2	1.9
Al₂O₃	0.36 - 2.60	25.0	-
Na₂O	0.01 - 1.35	12.5	-
K₂O		6.3	-
Fe₂O₃	0.01 - 0.70	-	70.0
Fe₃O₄	-	-	17.0
FeO	-	-	7.8
MnO	-	-	0.66
CaO	0.01 - 0.60	-	-
MgO		-	-

6.3.2 Experimental characterisation of slag conditioners

In order to obtain the physicochemical characteristics of the raw materials that are candidates for defoaming additives and slag conditioners, the following experimental techniques were employed:

- Particle size distribution: Obtained by sieving the samples using granulometric sieves manufactured by Abronzinox, with ASTM meshes of 5/16", 1/4", 3.5, 4, 5, 6, 7, 8, 10, 12, 14, 16, 18, 20, 30, 40, 60, and 200;
- X-Ray diffraction (XRD): Performed on an Anton Paar XRDynamic 500 diffractometer, with Mo-K α radiation, operating at 50mA and 55kV, with a goniometer diameter of 200 mm, and Bragg-Brentano geometry (reflection). Rietveld refinement of the diffractograms was performed using TOPAS software version 4.2, developed by Bruker;
- Micrographs and chemical mapping: Obtained on a TESCAN MIRA Scanning Electron Microscope (SEM), in backscattered electron mode with an

acceleration voltage of 25kV and working distance of 10-15mm. The samples were coated with a 10nm layer of AuPd alloy.

6.4 Results and discussion

6.4.1 Evaluation of the base slag by isothermal solubility diagram (ISD)

Considering the base slag from Table 6.1, and as discussed in the Methodology section, its composition presents a binary basicity of 3.5 and significant variation in FeO content. Thus, an interesting visualisation for the EAF is the Isothermal Stability Diagram (ISD), which was constructed for this system disregarding sulphur (S), considering the average contents of the minor oxides Al_2O_3 , MnO , P_2O_5 and TiO_2), and fixing the binary basicity. Presented in Figure 6.4, with the red dots representing the seven composition measurements as a function of FeO and MgO contents, the diagram highlights that the slags are in the MgO saturation field, reducing the tendency to attack dolomitic refractories. Furthermore, the presence of solids leads to an increase in effective viscosity, allowing for the formation and maintenance of foaming slag. Therefore, the next tests sought to understand the effect of a commercial additive on slag defoaming when tapped from the furnace to the pot.

6.4.2 Characterisation of a commercial CaF_2 -based defoaming agent

In order to understand the effect of a commercial additive on slag properties, the material available in the form of briquettes (Figure 6.5a) was characterised regarding its chemical and mineralogical composition. Figure 6.5b presents the macrostructure of a briquette with a 2.2 x 1.4 cm section, showing chemical homogeneity due to the low variability of grey tones, except for the lighter particles, which will be subsequently identified as magnetite (Fe_3O_4).

Complementarily, EDS mapping was performed on a surface region of the sample (Figure 6.6a) and a bulk one (Figure 6.6b). These micrographs reinforce the macroscopic homogeneity observed in the briquette, with the main difference between them being the presence of magnetite particles. Furthermore, the presence of SiO_2 and CaF_2 aggregates is also evident, with the other identified elements distributed in the matrix. The

composition of aggregates 1 to 6 highlighted in Figure 6.6 can be compared with the point EDS analysis, presented in Table 6.3.

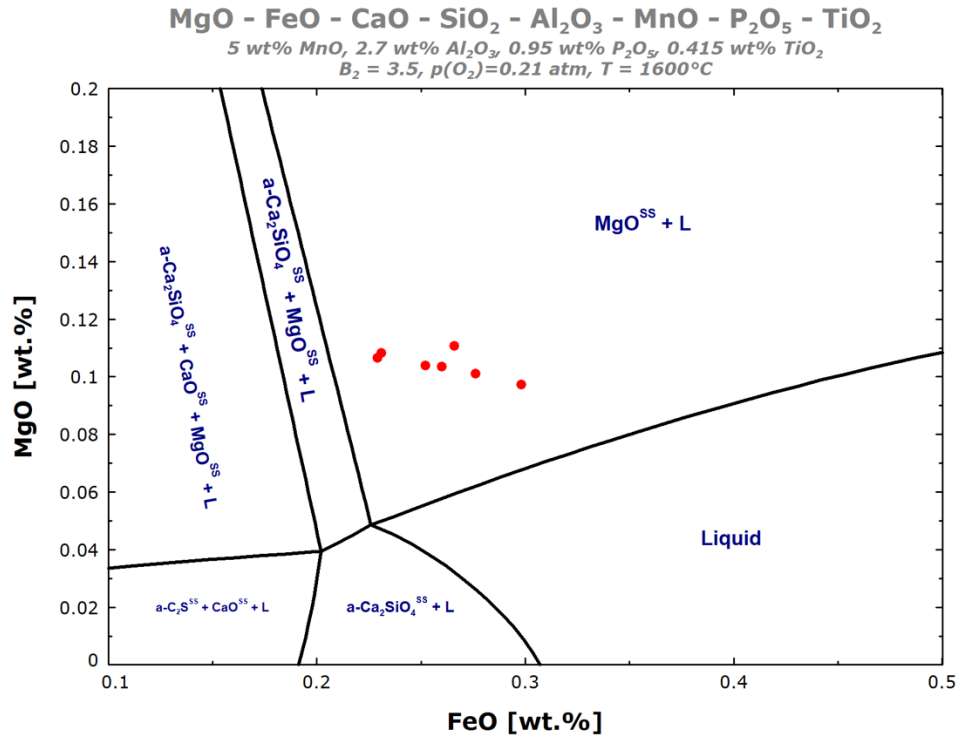


Figure 6.4: Isothermal solubility diagram (ISD) for the base slag.

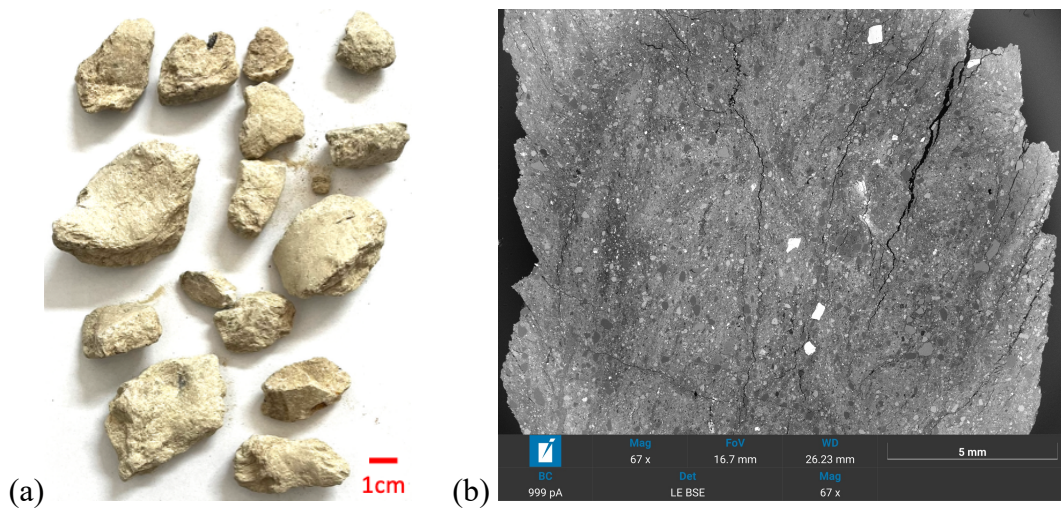


Figure 6.5: (a) Commercial briquettes for EAF slag defoaming and (b) backscattered electron macrograph.

EDS mapping was also performed using higher magnification in the central region of the briquette, with individual channels for Ca, Si, Fe, Mg, Al, F and O presented in

Figure 6.7. In addition to corroborating the presence of silica and magnetite particles, this analysis highlights that the briquette matrix is formed by fines of Ca, Mg, Fe and Al, demanding an X-ray diffraction analysis to identify the constituent phases.

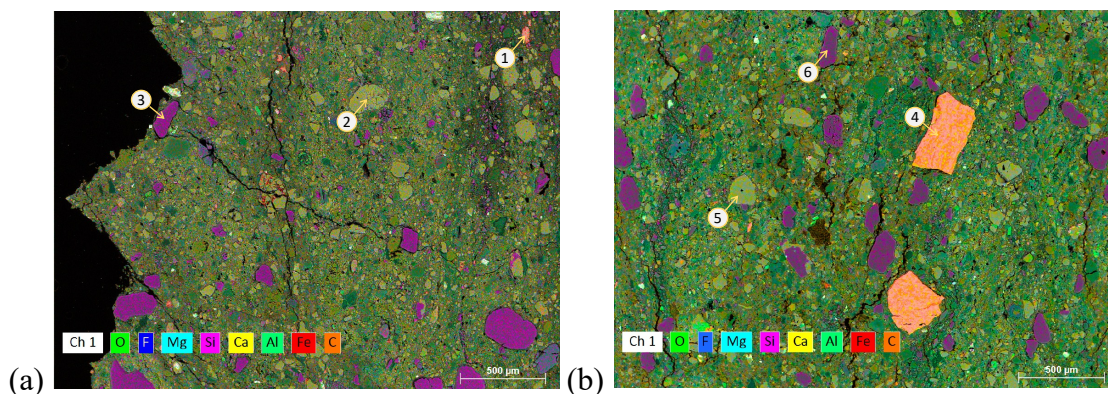


Figure 6.6: Micrographs with EDS mapping of the (a) surface and (b) bulk regions of the commercial briquette.

Table 6.3: Atomic composition from point EDS analysis.

Point	Fe	Ca	Si	Na	Sr	O	F	S
(1)	70.9	2.3	-	-	-	26.8	-	-
(2)	-	53.0	-	-	-	1.2	45.8	-
(3)	-	-	51.6	-	-	48.4	-	-
(4)	60.8	0.8	0.3	0.4	-	37.7	-	-
(5)	-	43.3	0.2	-	-	8.1	48.3	-
(6)	-	0.4	51.0	-	0.2	46.9	-	0.2

Analysing the X-ray diffraction spectra from the ground and sieved briquette sample, and quantifying the phases by Rietveld refinement, the weight proportion was obtained as presented in Table 6.4. From this analysis, the presence of fluorite (CaF_2), quartz (SiO_2), and magnetite (Fe_3O_4) is evident, as anticipated by the micrographs with EDS mapping. Also, calcium is present in the form of carbonate (CaCO_3) and hydroxide [$\text{Ca}(\text{OH})_2$], in addition to the presence of magnesium hydroxide ($\text{Mg}(\text{OH})_2$).

When comparing the results of EDS mapping and XRD quantification, it is worth noting the limitations of each technique. The former is conducted in specific regions of the sample, and although Figure 6.6 presents surface and bulk regions, it is still limited to a single briquette sample and a limited area. On the other hand, the XRD analyses a more

representative volume of the sample, but the phase quantification is still limited by the performance of the Rietveld refinement. For instance, León-Reina *et al.* (143) investigated the accuracy of quantification using synchrotron powder diffraction, yielding a relative error of 20% for concentrations above 1.0 wt%. Thus, the discrepancy between Figure 6.6 and Table 6.4 in the quantities of minor phases (Fe_3O_4 and SiO_2) may be related to inhomogeneities in phase distribution and limitations of the characterisation techniques, as lab-scale equipment was employed in this work.

Therefore, the analysed commercial solution is mostly composed of fluorite (CaF_2), a compound with mixed effects on slag foamability. As reported by Kim *et al.* (144), concentrations up to 5 wt.% reduced slag foamability in the $\text{CaO-SiO}_2\text{-FeO-MgO}$ system, associated with a decrease in viscosity. On the other hand, foamability rises again with CaF_2 concentrations above 5%, which the authors associated with the drop in surface tension due to its high content. That is, this result reinforces this compound as a defoaming agent, provided its proportion is correctly adjusted.

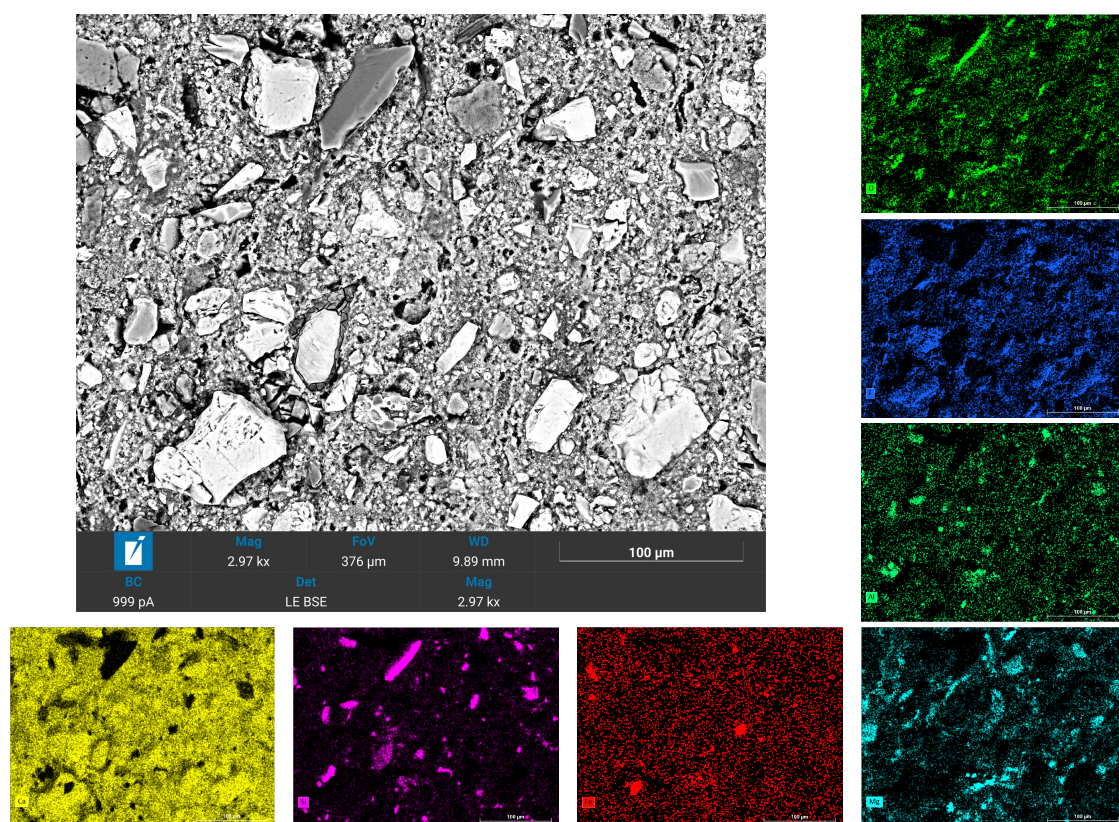


Figure 6.7: Micrograph of the bulk region of the commercial briquette with individual EDS mappings of Ca, Si, Fe, Mg, Al, Fe, and O.

Table 6.4: Phases in the commercial briquette after X-ray diffraction identification and Rietveld refinement.

Mineralogical phase	Chemical formula	wt. %
Fluorite	CaF_2	79 %
Calcite	CaCO_3	8 %
Portlandite	Ca(OH)_2	4 %
Quartz	SiO_2	4 %
Brucite	Mg(OH)_2	4 %
Magnetite	Fe_3O_4	1 %

However, the search for alternative slag conditioners has gained importance with the restriction on the use of fluorides in steelmaking, both due to operational problems that can lead to localised wear in the refractory lining (145,146) and occupational risks due to the generation of hydrofluoric acid (HF) (147,148). To this end, it is essential that the effect of potential additives on the physical properties of the slag can be modelled and predicted, reducing the demand for laboratory experiments and industrial tests.

6.4.3 Assessing the briquette effect on foaming slag

Considering that the characterised additive is commercialised as a solution for defoaming EAF slags, the next step consisted of predicting its effect using the methodology developed in Chapter 5. Thus, the phase proportions from Table 6.4 were considered to construct the phase stability diagram presented in Figure 6.8, indicating the effect of adding the briquette to the average slag composition (Table 6.1). This result is plotted so as not to normalise the product obtained to 100%, indicating the increase or decrease caused by the additive in the mass of each of the phases present in the slag. It is also worth noting that this graph is obtained at a temperature of 1500°C, considering that there is a temperature drop between the EAF and the slag pot.

Thus, it can be noted in Figure 6.8 that the main effect of the commercial briquette is the consumption of calcium silicate (C_2S), with up to 4 wt.% of additive, and periclase (MgO), leading to the formation of liquid. Thus, a drop in the effective viscosity of the slag is expected, accelerating the foam ageing process. Another phase present is the gas, whose chemical composition was also extracted in Figure 6.8 for components above 0.1

wt.%. In this result, the generation of CO_2 and H_2O is noted - originating from the decomposition of calcium carbonate and calcium and magnesium hydroxides - in addition to the generation of HF , reinforcing the occupational risk in the use of fluorides in high-temperature processes.

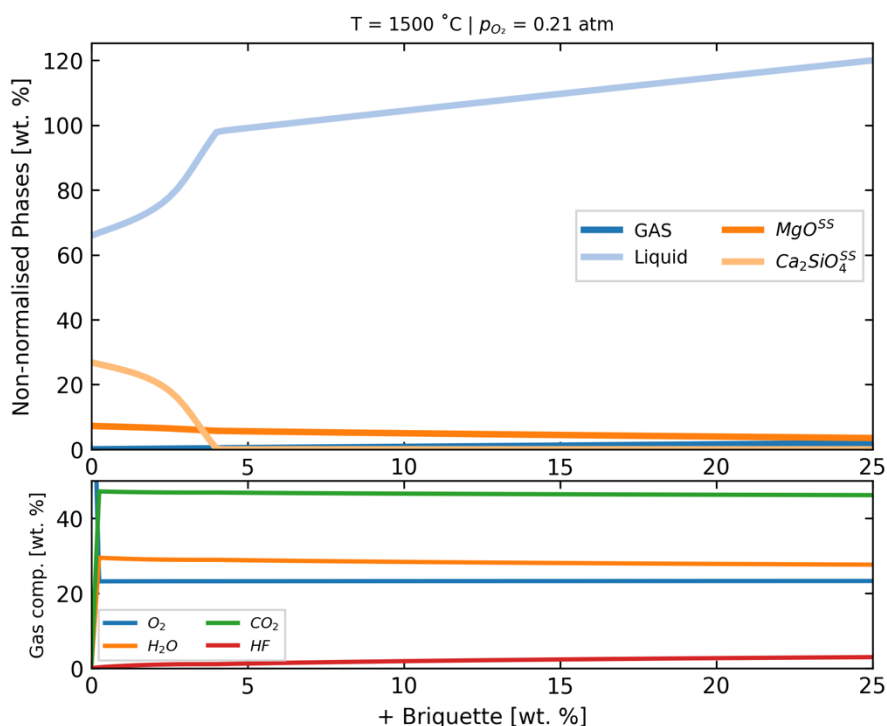


Figure 6.8: Phase stability as a function of the addition of the commercial briquette (mainly CaF_2) up to 25 wt.%, and the composition of the formed gas.

Based on the composition of the liquid slag fraction obtained by thermodynamic calculation, its physical properties of density, surface tension, and effective viscosity can be predicted, as presented in Figure 6.9. In this figure, the surfactant role of fluorite is observed, lowering the surface tension with small additions. There is also a density reduction effect, mainly during the consumption of C_2S . The greatest variation is in the effective viscosity, having its value reduced by the consumption of solid phases (C_2S and MgO). However, when observing the viscosity behaviour for the liquid fraction (light green line), there is an opposite trend of increasing this property up to about 4 wt.% of the additive. This is caused by the increase in CaO and SiO_2 contents during calcium silicate consumption. Comparing with Figure 6.8, 4 wt.% of the briquette was sufficient

to solubilise the 27 wt.% of C_2S in the slag. That is, this fraction of additive brought 8.7 wt.% of CaO and 18.3 wt.% of SiO_2 to the liquid fraction of the slag, raising its viscosity (μ_{liq}), but still not enough to compensate for the loss of the solid fraction, which contributes to the lowering of the effective viscosity (μ_{eff}).

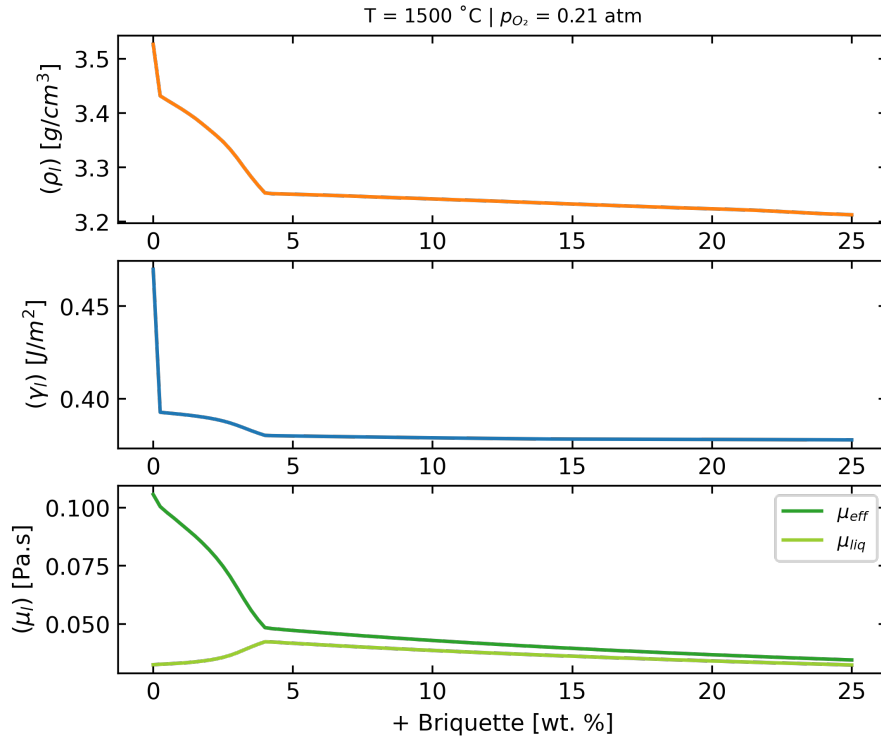


Figure 6.9: Predicted effect of the commercial briquette on the properties of the slag.

The relative impact on the ageing times of the foaming slag was calculated based on the properties of Figure 6.9 and is presented in Figure 6.10. Considering an addition of 4 wt.% of commercial briquette, it is noted that the drainage and coalescence mechanisms are favoured, with a reduction of approximately 50% in both, primarily impacted by the drop in effective viscosity. Only the coarsening mechanism exhibits an increase in its characteristic time due to the lower surface tension. Therefore, it can be said that the main mechanism of action of the commercial briquette lies in the reduction of effective viscosity, even compensating for the reduction in density and surface tension.

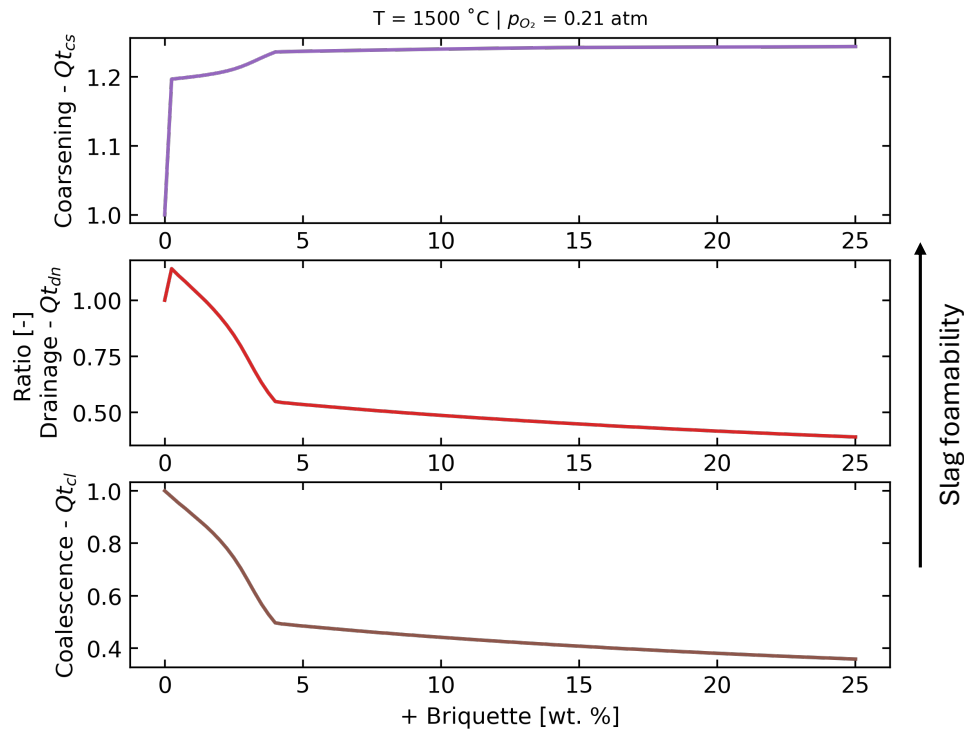


Figure 6.10: Predicted effect of the commercial briquette on the ageing times of foams.

6.4.4 Evaluation of alternative defoaming conditioners for slags

When evaluating an alternative slag conditioner, the chemical and thermal aspects involved in its use must be considered. Regarding the latter, the phase stability of the slag (average composition) as a function of temperature can be evaluated, as presented in Figure 6.11 for 1000 to 2000 °C. Thus, considering a temperature drop from 1600 °C in the EAF to 1500 °C in the slag pot, a significant increase in the solid fraction would be expected (from 5 to 34 wt.%) mainly due to the precipitation of C_2S , leading to a higher effective viscosity of the slag and consequently greater stability of the foam generated in the electric furnace. However, a subsequent reduction of 100 °C in the slag temperature, to 1400 °C, would cause an increase of only 6 wt.% in the solid fraction. That is, even if the candidate additives lead to a reduction in slag temperature in the pot, their effect would be marginal. Therefore, only the chemical effect was considered, maintaining the temperature constant at 1500 °C to obtain the composition of the resulting liquid fraction of the slag. Next, the following potential additives will be investigated: silica sand, sodalite, and steel scale.

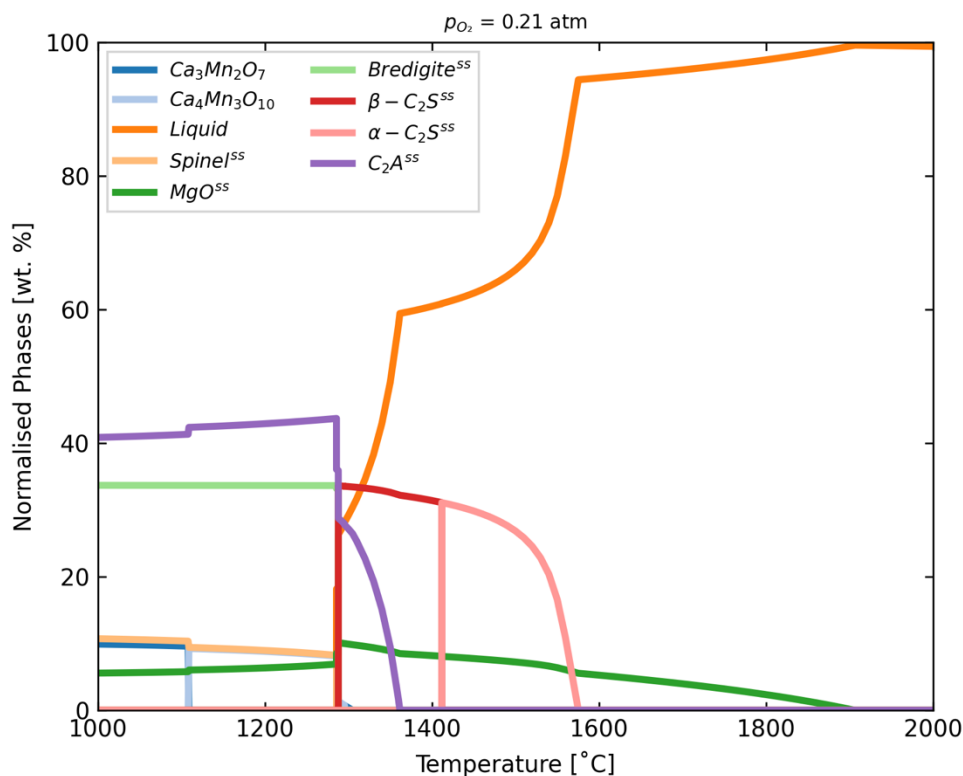


Figure 6.11: Phase stability in the average composition of the slag under study.

The first additive investigated was silica sand, composed mostly of SiO_2 , according to the chemical composition indicated in Table 6.2, so minor impurities were disregarded for this analysis. Thus, Figure 6.12 presents the effect of silica addition on the phase stability of the slag under study, where an initial increase in the C_2S fraction is noted up to 6.2 wt.% of added sand. From this point on, and considering the high basicity of the slag, the addition of more SiO_2 leads to the consumption of C_2S and MgO , becoming completely liquid above 10.5 wt.% of additive.

Using the chemical composition of the liquid slag fraction, the effect of SiO_2 addition on physical properties was predicted and is presented in Figure 6.13, showing a reduction in density and surface tension. Again, the effective viscosity shows a combined effect of solid fraction reduction with the increase in liquid viscosity, probably due to higher SiO_2 contents. Thus, it is expected that foam ageing will be accelerated as long as the consumption of precipitated phases occurs, mainly calcium silicate. However, from the moment the slag becomes completely liquid, the additive then has an opposite effect on the collapse of the foaming slag.

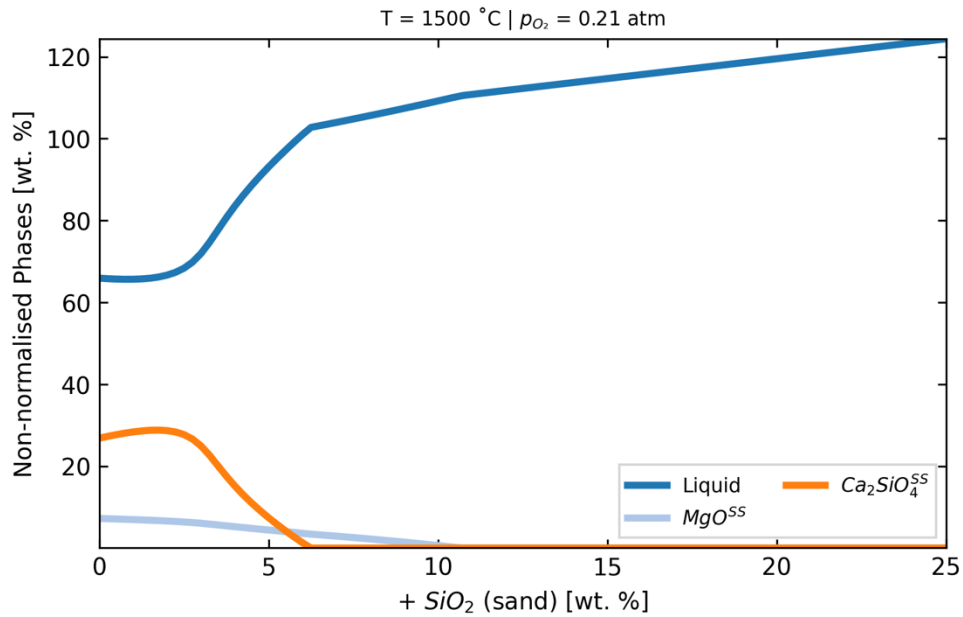


Figure 6.12: Phase stability as a function of the addition of SiO_2 sources (e.g., silica sand) up to 25 wt.%.

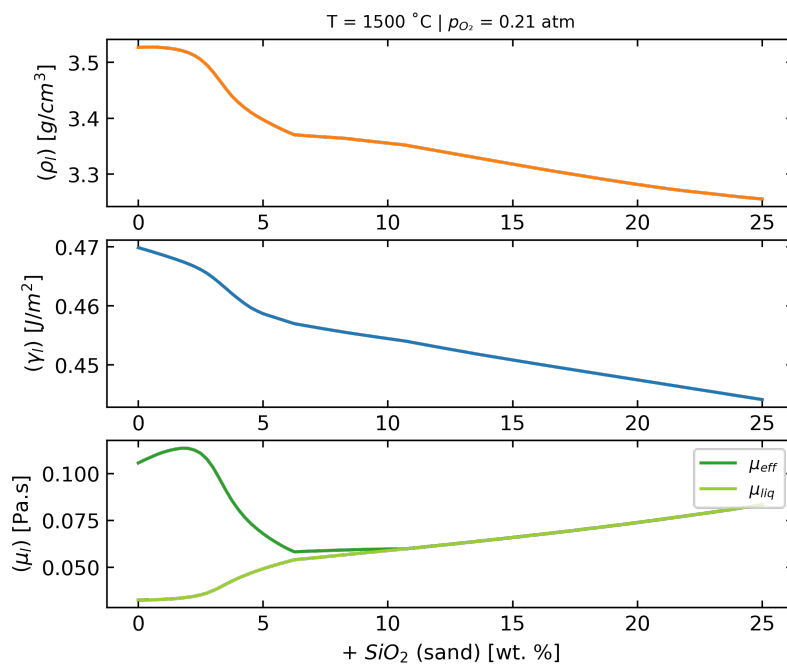


Figure 6.13: Predicted effect of SiO_2 on the physical properties of the slag.

This discussion can be confirmed by the combined effect of properties on characteristic times, according to the result presented in Figure 6.14. In this figure, it is possible to note that up to 6.2 wt.% of SiO_2 would accelerate the drainage and bubble

coalescence mechanisms, with a 40% reduction in t_{dn} and t_{cs} (acting to collapse the foaming slag), while only the coarsening mechanism would be delayed by about 3%. However, for additions above 6.2 wt.% of SiO_2 , all three mechanisms would be disfavoured, presenting no advantages from the perspective of foam destabilisation.

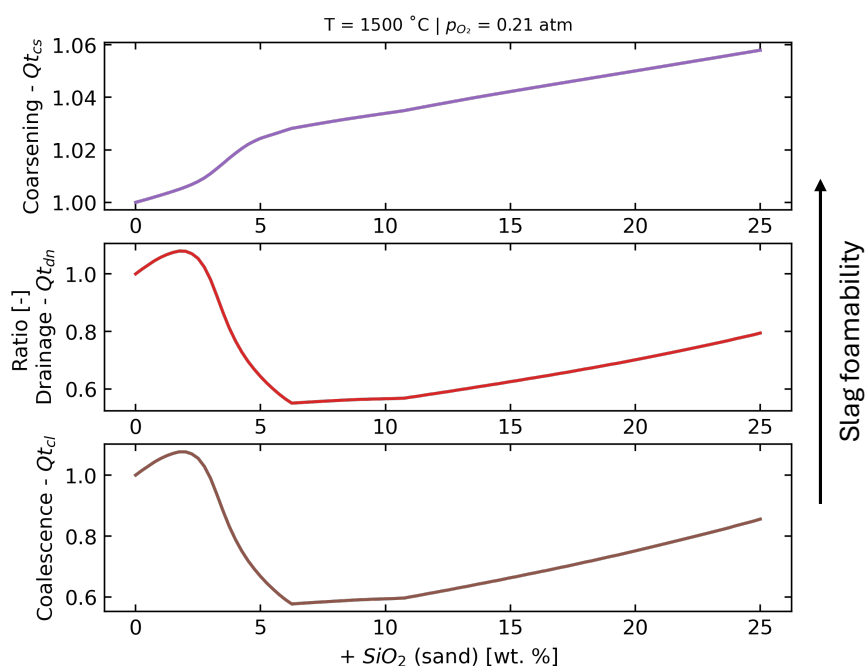


Figure 6.14: Predicted effect of SiO_2 on the ageing times of the foaming slag.

The second additive considered was sodalite, according to the chemical composition indicated in Table 6.2. Its effect on slag phase composition is evaluated in Figure 6.15, demonstrating a consumption of solid phases (C_2S and MgO) from the beginning of sodalite addition. In this sense, 6.2 wt.% of the additive is required to solubilise all the calcium silicate present, while 17.5 wt.% would be required for the slag to become completely liquid.

Evaluating the impact of sodalite on the chemical composition of the liquid slag fraction and, consequently, on its physical properties, Figure 6.16 is obtained. Bearing in mind that more than 50% of the sodalite composition is SiO_2 , it is worth noting that the drop in density is equivalent to that observed in Figure 6.13. On the other hand, the presence of alkalis (Na and K) causes the drop in surface tension to be more significant, which can act to stabilise the foam. Regarding viscosity, the effect of SiO_2 in increasing

the viscosity of the liquid fraction is again observed, while the consumption of the solids present causes the effective value to be reduced.

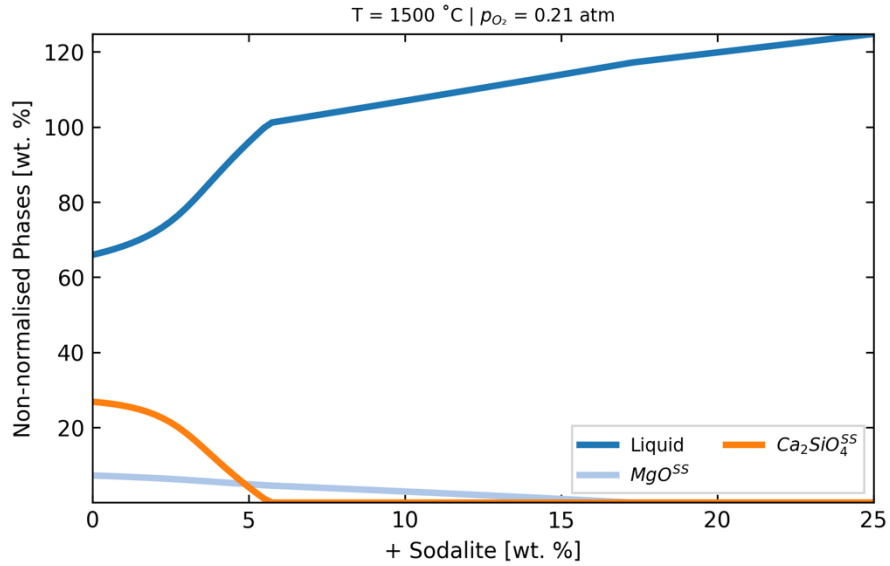


Figure 6.15: Phase stability as a function of sodalite addition up to 25 wt.%.

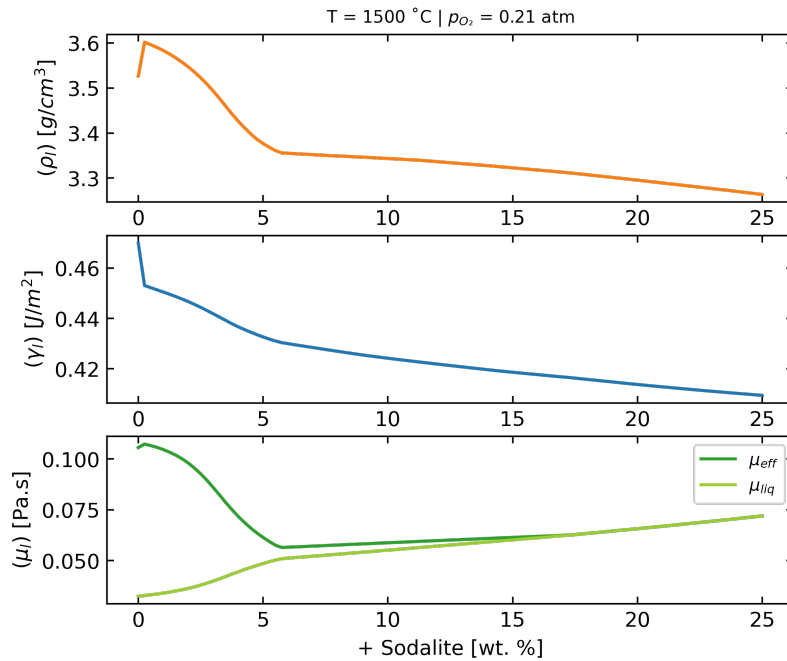


Figure 6.16: Prediction of the effect of sodalite on the physical properties of the slag.

Applying the physical property values to the characteristic foam ageing times in Figure 6.17, a similar result as for the addition of silica sand is noted. Up to 5.8% added

sodalite causes the drainage and coalescence mechanisms to be accelerated, reducing t_{dn} and t_{cs} by over 40%. From this point on, all three mechanisms become disfavoured, increasing the foam lifespan. Furthermore, the drop in slag surface tension causes the coarsening mechanism to be delayed, resulting in a 9% increase in t_{cs} with 5.8 wt.% sodalite added – compared to the 3% increase for SiO_2 as an additive (Figure 6.14). Therefore, the use of sodalite compared to silica sand does not demonstrate significant advantages, as the content required for an equivalent effect on ageing times is marginally lower (about 0.4 wt.%). Additionally, the high variability of sodalite as a raw material must be considered, which would hinder process stability.

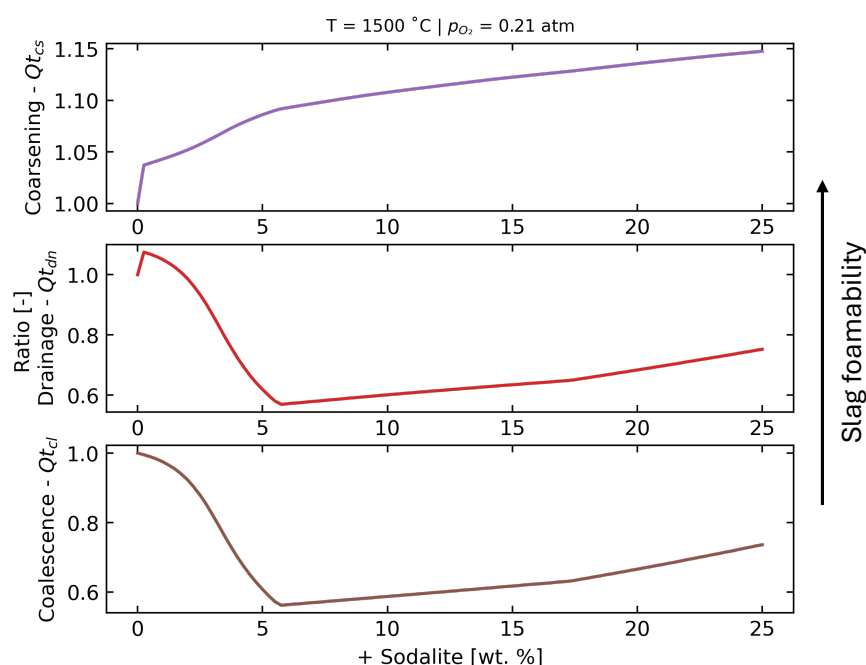


Figure 6.17: Prediction of the effect of sodalite on the ageing times of foams.

Finally, the effect of steel scale on foaming slag stability is evaluated, according to the chemical composition in Table 6.2. Depending on the steel plant under consideration, this raw material presents itself as an available byproduct of the rolling area, being a low-cost raw material. Its effect on the phase composition of the slag under study can be observed in Figure 6.18, requiring 15.5 wt.% of additive for the consumption of calcium silicate and solubilization in the slag. For the entire slag to become liquid, the amounts required would be greater than 25 wt.% of scale.

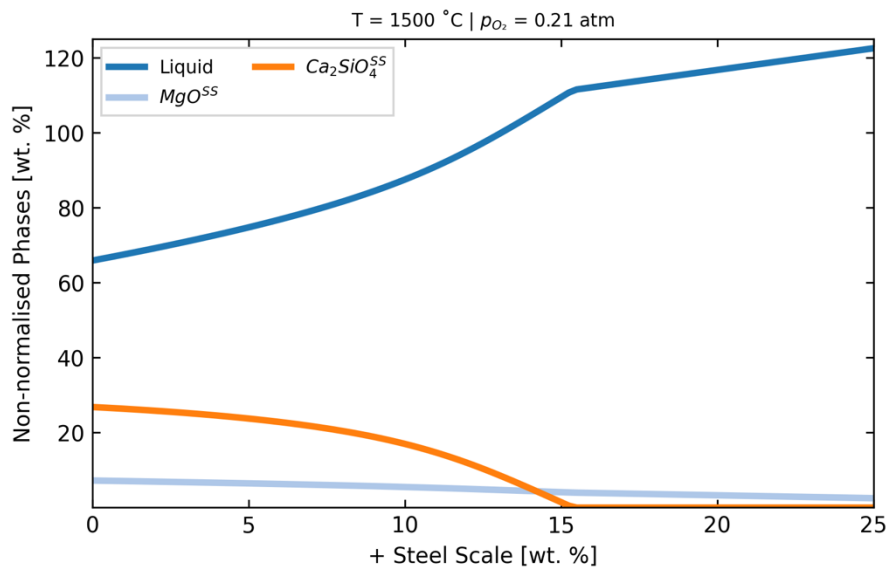


Figure 6.18: Phase stability as a function of steel scale addition up to 25 wt.%.

From the point of view of slag physical properties, and as presented in Figure 6.19, steel scale demonstrated little effect on the density and surface tension of the liquid fraction. On the other hand, comparing this result with the viscosity of the liquid fraction in Figure 6.16, it is noted that the increase caused by C_2S consumption is more controlled, so that the effective viscosity is reduced below 50 mPa.s, and continues to decay for higher additive contents. That is, the main effect of adding scale would be the sustained lowering of the effective viscosity, accelerating the collapse of the foaming slag.

Consequently, it can be observed in Figure 6.20 that the coarsening mechanism has almost no variation (within an amplitude of 0.8%), given that the surface tension is practically constant. On the other hand, the drainage and coalescence mechanisms are significantly impacted by slag viscosity, requiring about 10 wt.% of additive for such characteristic times to be reduced by 40% (an effect equivalent to a content of 6.2 wt.% SiO_2 , according to Figure 6.14). However, increasing the additive content to 15.5 wt.%, it is still possible to reduce t_{dn} and t_{cl} by 60% of the original value. That is, despite requiring a greater mass of steel scale to achieve the same result as silica sand, it presents a greater potential in accelerating the foam ageing mechanisms. Therefore, this additive was selected for an in-depth investigation, including the experimental characterisation of the raw material for more assertive predictions.

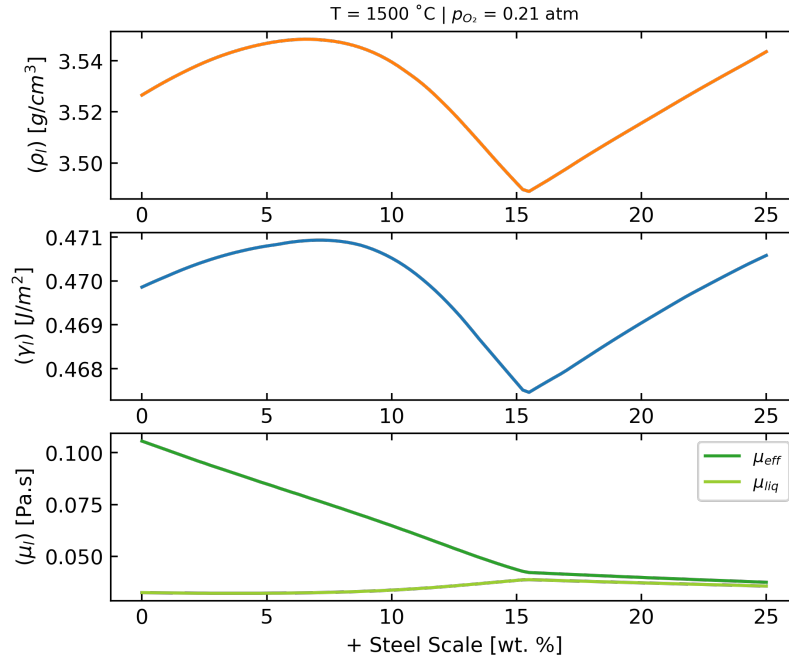


Figure 6.19: Prediction of the effect of steel scale on the physical properties of the slag.

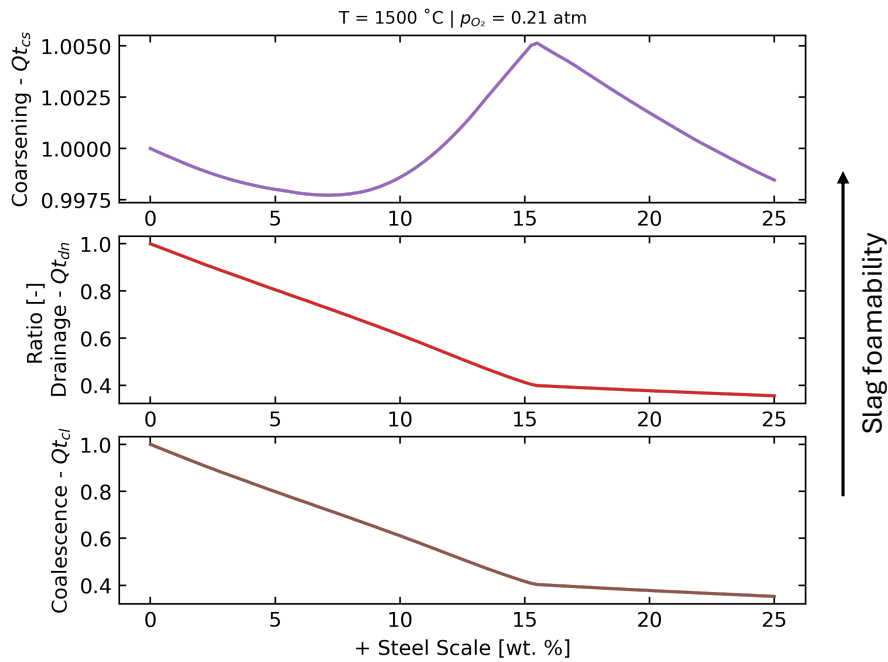


Figure 6.20: Prediction of the effect of steel scale on the ageing times of foams.

6.4.5 Characterisation of the cooling bed's steel scale

Considering the potential effect of steel scale on the collapse of EAF foaming slags, the study proceeded to an evaluation of operational viability, facing some

challenges related to the presence of water and machine oil originating from the rolling process. Thus, an alternative with similar chemical composition would be the steel scale generated in the cooling bed of the continuous casting, where contact with moisture and oils is limited. Two samples, as presented in Figure 6.21, were collected for analysis. Visually, and as expected by the detachment of scale from the bars, it is noted that such material presents itself in the form of platelets, with sizes varying from millimetres to fines. Therefore, a characterisation of the size distribution and mineralogical composition was performed.

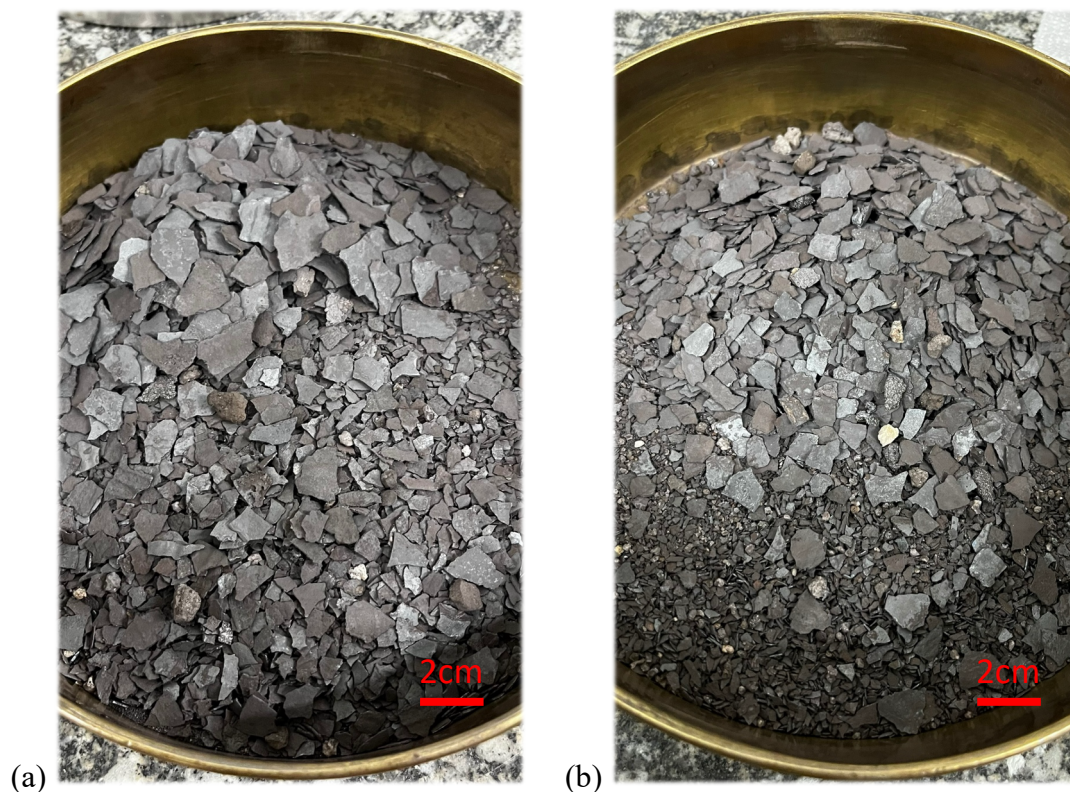


Figure 6.21: Visual aspect of the two samples collected from the cooling bed of the continuous casting.

Figure 6.22 presents the particle size distribution for the two steel scale samples, confirming their distribution from below $75\ \mu\text{m}$ to larger than $8\ \text{mm}$. This result can be interpreted in conjunction with the mineralogical composition presented in Table 6.5, obtained by X-ray diffraction analysis and Rietveld refinement. In this case, two fractions were analysed: fines below $75\ \mu\text{m}$ and the range between $75\ \mu\text{m}$ and $3.35\ \text{mm}$, which would be suitable for handling in the steel plant. Based on this result, the scale is

composed of a combination of iron oxides in different oxidation states (Fe_2O_3 , Fe_3O_4 , and FeO), with Magnetite being the main component, with 62 wt.% for the intermediate fraction. In the fine fraction, a considerable concentration of carbon (elemental or contained in a phase) stands out, which could lead to gas formation when added to the slag, promoting its foaming. On the other hand, the intermediate range presents a carbon content at the detection limit of the method (0.3 wt.%), avoiding the generation of CO bubbles. Therefore, when applying this steel scale as a defoaming agent, the separation of such fines that could increase the carbon concentration would be interesting.

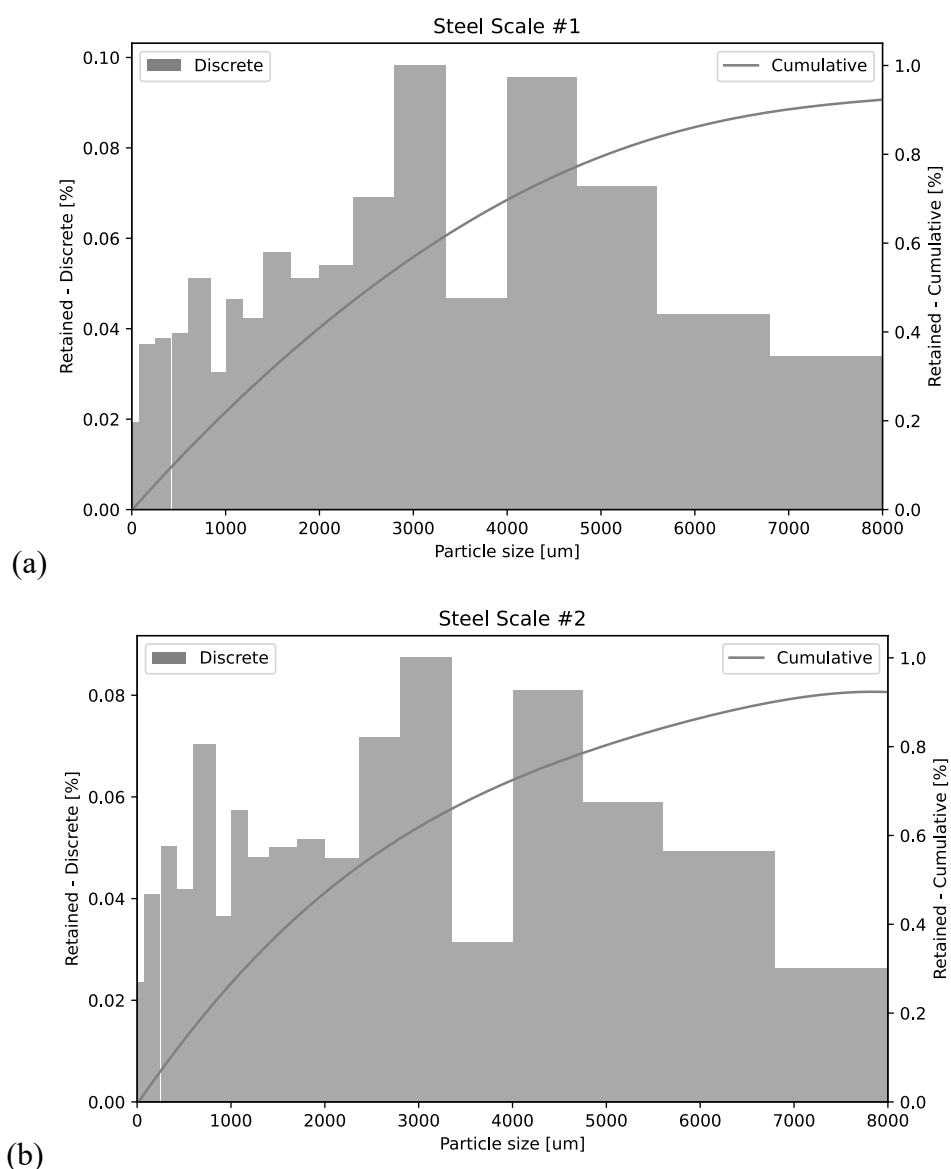


Figure 6.22: Particle size distribution for the two samples collected from the continuous casting cooling bed.

Table 6.5: Phases in the sample collected from the bar cooling bed, identified using X-ray diffraction and Rietveld refinement.

Mineralogical phase	Chemical formula	wt.%	
		< 75 μ m	75 μ m-3.35mm
<i>Hematite</i>	Fe ₂ O ₃	45.1	17.0
<i>Magnetite</i>	Fe ₃ O ₄	40.6	61.5
<i>Wuestite</i>	FeO	6.4	21.2
<i>Graphite</i>	C	5.2	0.3
<i>Khamrabaevite</i>	TiC	2.6	-

Given that the proportions of iron oxides in the steel scale from the continuous casting and the rolling mill differ, the next step consists of predicting the effect of such an additive on the slag composition under study. The result is presented in Figure 6.23, from which it is possible to note that the same 15.5 wt.% of scale would be demanded for all the calcium silicate precipitated in the slag to be consumed. Furthermore, considering the composition of the liquid slag fraction, the effect of the steel scale on the characteristic foam ageing times is presented in Figure 6.24, where it is evident that the drop in times for the drainage and coalescence mechanisms is repeated, reducing them by up to 60%, while coarsening remains practically constant.

Another scenario in which the additive can be evaluated before the proper industrial test is regarding atmospheres deprived of oxygen for reaction. Although the transfer of foaming slag to the pot occurs in an open atmosphere, the kinetics for the slag-atmosphere reaction must be considered, as well as the fact that the slag-additive equilibrium may happen in the pot volume without reaching equilibrium with the atmosphere. Therefore, calculations were also performed without setting the partial pressure of oxygen, so that the system itself seeks equilibrium with the gas formed. This result is presented in Figure 6.25, where a higher initial liquid fraction can be observed when compared with Figure 6.23 (79 wt.%, against 66 wt.%), as well as different C₂S and MgO contents, and the presence of CaO.

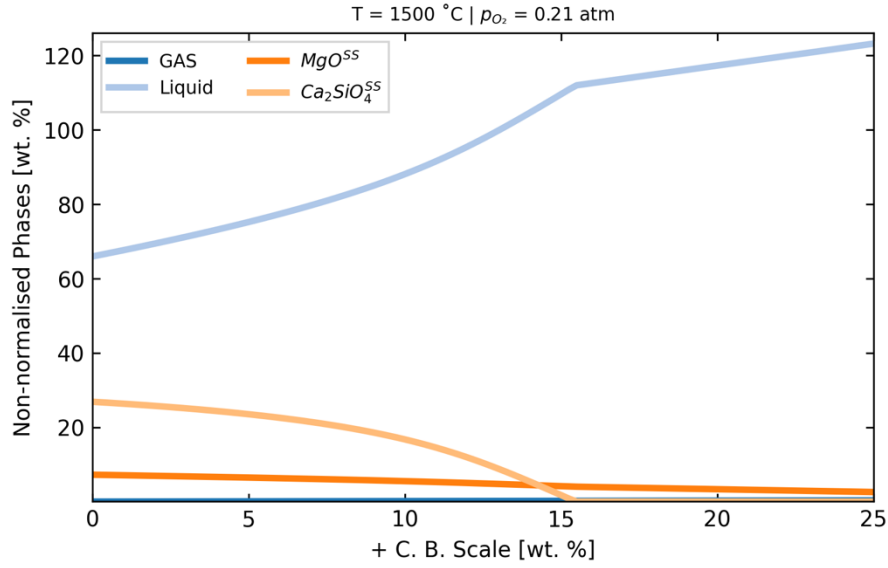


Figure 6.23: Phase stability as a function of the addition of steel scale from the cooling bed up to 25 wt.%, in an oxidising atmosphere.

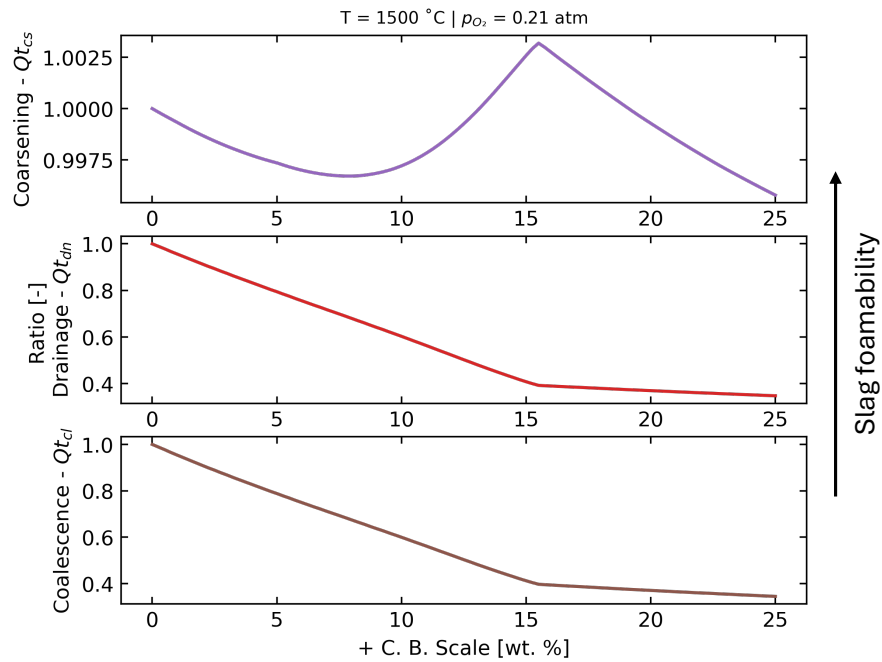


Figure 6.24: Prediction of the effect of the steel scale from the cooling bed on the characteristic ageing times of foams, under oxidising atmosphere.

Evaluating the effect of not defining the atmosphere on the physical properties of the slag, as presented in Figure 6.26, it is possible to note that density and surface tension properties tend to increase with the addition of the steel scale. Furthermore, the effective

viscosity has a downward trend, influenced by both the less viscous liquid (μ_{liq}) and the consumption of solid phases. That is, all three properties act in the direction of destabilising the foam, accelerating its ageing and collapse process.

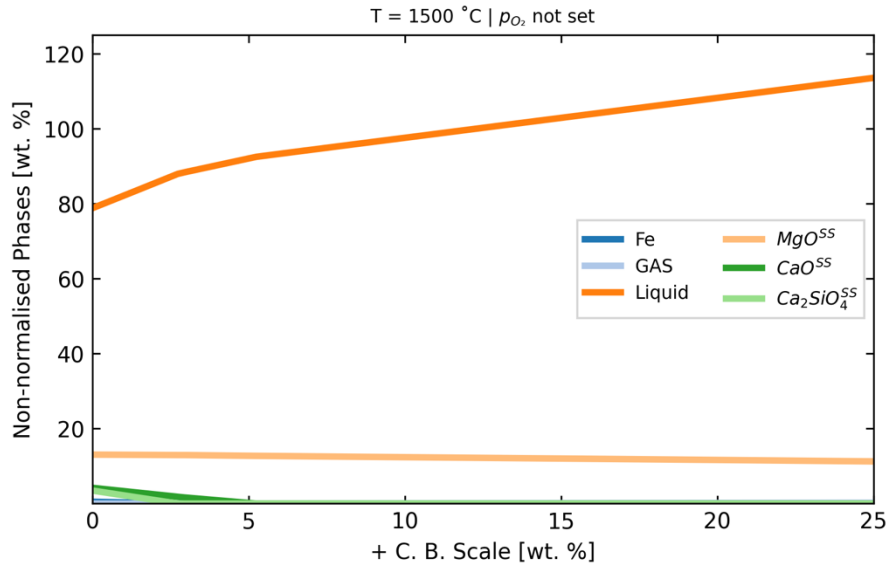


Figure 6.25: Phase stability as a function of the addition of steel scale from the cooling bed up to 25 wt.%, without a set atmosphere.

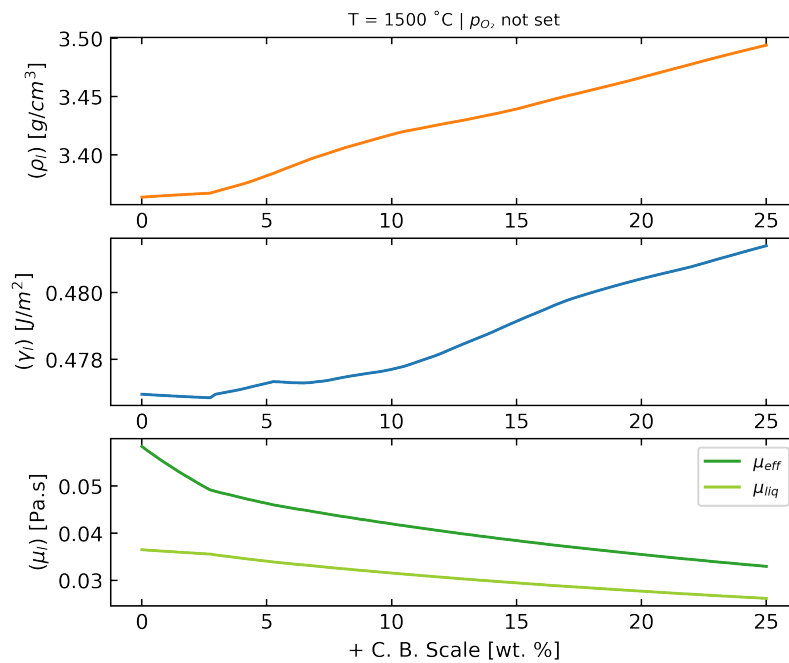


Figure 6.26: Predicted effect of steel scale on slag properties, without a set atmosphere.

Lastly, applying such properties in the prediction of characteristic foam times, a general downward trend can be noted, making the foam less stable in Figure 6.27. Even so, the time for the coarsening mechanism reduces by less than 1%, given that the change in surface tension is not significant. Furthermore, despite the drop in drainage and coalescence times, the 25 wt.% of the additive considered still does not evaluate the lowest value that can be obtained, given that there would still be about 11 wt.% of solid MgO in the slag. Analysing the effect of 15.5 wt.% of additive on t_{dn} and t_{cs} , the reduction would be approximately 25% in times, lower than the 60% obtained under an oxidising atmosphere.

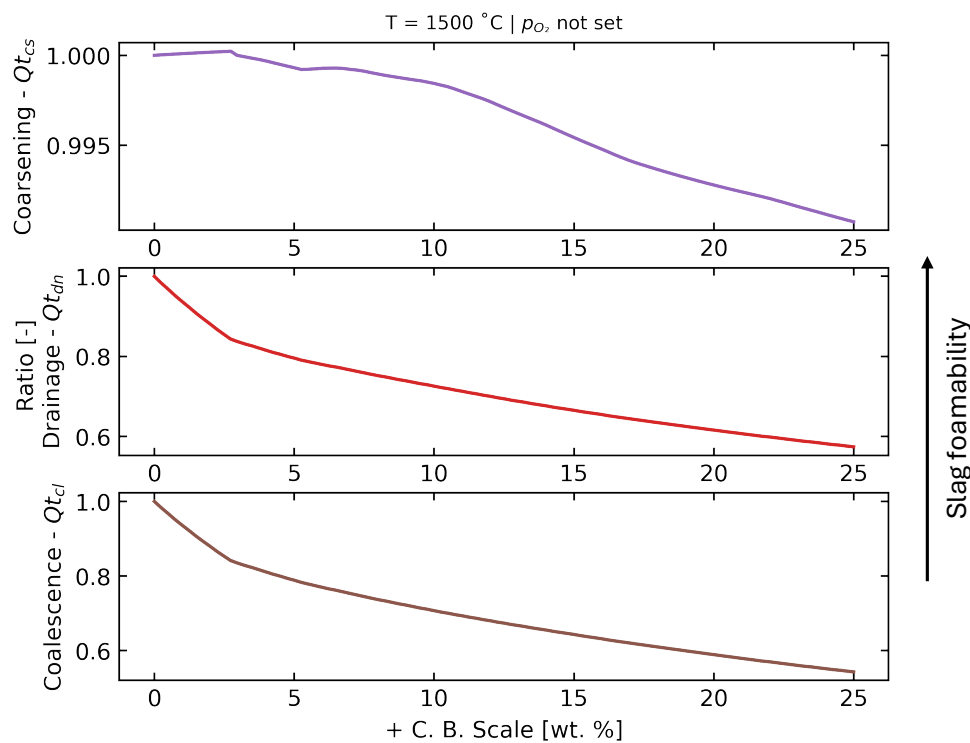


Figure 6.27: Predicted effect of steel scale on the ageing times of foams, without a set atmosphere.

Therefore, the set of results for the effect of the steel scale from the cooling bed shows that this additive has the potential to destabilise EAF slag. However, the importance of the oxidising atmosphere in such a process must be observed, such that an emulsion between foaming slag, scale, and atmospheric air incorporation is desired.

6.5 Conclusion

The control of foaming slags is a steelmaking challenge both to ensure greater stability during primary refining in the EAF, and to accelerate the collapse of the foam during its disposal, as to contain its volume in the slag pot. Focusing on the defoaming of slag originating from the EAF, this work investigated the effect of a commercial additive and potential alternative raw materials, predicting the characteristic times of foam ageing mechanisms - namely coarsening, drainage, and bubble coalescence.

Regarding the commercial additive, its experimental characterisation indicated a high concentration of fluorite (80 wt.%), with CaF_2 having effects of lowering viscosity and surface tension. In this case, while lower viscosity promotes the collapse of foaming slag, surface tension tends to increase foam stability. This effect was evident in the characteristic ageing times of the slag, with up to 4 wt.% of the briquette significantly favouring drainage and coalescence, while coarsening was controlled. However, the use of fluorine in plants operating at high temperatures is associated with occupational problems due to HF formation.

As alternative defoaming additives, the use of silica sand, sodalite, and steel scale was investigated. Considering that the first two raw materials have high silica contents (above 95 and 56 wt.%, respectively), their main effect was the consumption of calcium silicate (C_2S) and reduction of the effective viscosity of the slag. On the other hand, the higher SiO_2 content in the slag leads to an increase in the viscosity of the liquid fraction, as well as a drop in surface tension and density. Therefore, the effect ceases to be beneficial as soon as the solid phase is consumed, which occurs with 5.8 and 6.2 wt.% of sand and sodalite, respectively. In turn, steel scale presented a sustained drop in the effective viscosity due to the dissolution of C_2S and MgO phases, maintaining density and surface tension practically constant. Although a larger additive fraction is required (10 wt.%) to achieve the same effect as 5.8 wt.% of sodalite, the availability of this raw material in steel plants motivated a more in-depth experimental investigation.

To analyse the viability of steel scale (collected from the continuous casting bar cooling bed) as a defoaming agent, its particle size distribution and mineralogical composition were characterised. These results indicated a concentration of carbon sources in the fines (below 75 μm), with the intermediate particle size (75 μm - 3.35 mm) being the most indicated for conditioning the foaming slag in the disposal pot. Based on the

phase composition obtained for the industrial steel scale, the effect of this composition on the characteristic ageing times of the slag was evaluated, confirming its contribution to foam collapse, mainly under oxidising conditions.

This example illustrates how the association between computational thermodynamics calculations (FactSage) and machine learning predictions (GlassNet) allows for the evaluation of alternative foaming (or defoaming) additives, such as steelmaking co-products and recycled raw materials.

CHAPTER 7 – GENERAL DISCUSSION AND CONCLUSION

This thesis investigated two of the multiple roles that bubbles play in the making of cleaner and greener steels, discussing the fundamentals of how to control the generation of bubbles, their influence on the kinetics of inclusion removal and how the slag properties affect their stability as a foamy layer. One thing to learn from the science of bubbles: although the interface holds so many unanswered questions, that is where boundaries are able to be pushed. In this work, for example, knowledge from aluminium foaming, froth flotation and glass science was borrowed as building blocks to understand the complexity of steelmaking.

Modelling the generation of bubbles in porous structures, four regions in the quasi-static regime became evident as the calculations were validated with experimental results. For low contact angles, the pore defines the bubble base and, consequently, the bubble size. For higher contact angles, the gas is able to expand over the bubbler surface, causing the bubble size to increase. In between, a transition region was observed where the dynamic contact angle limits the bubble base expansion. Also, for non-wetted surfaces, the superhydrophobicity induces a thin film of gas to be generated over the bubbler. These four regions support the understanding of bubbling gas into the ladle or tundish, where compositions for the purging plug are typically sought to avoid the infiltration by liquid metal. However, the drawback is the generation of large bubbles, beyond the upper limit of an optimum size to remove non-metallic inclusions.

The importance of having a bubble plume within the optimum region has been found in experimental pieces of evidence in the flotation experiments conducted in the water model. Firstly, a reliable experimental procedure was built to reproduce the bubble-induced flotation of inclusions using water and hollow glass particles, with a continuous measurement of particle concentration. Then, by varying the bubble size and gas flow rate, the effect of these parameters in the removal rates and maximum efficiency was investigated. Focusing on the former, bubbles within the optimum range confirmed the higher removal rates as collision and adhesion probabilities are favoured. As a trade-off, bubbles below the optimum size resulted in lower removal rates but, still, higher maximum efficiencies.

On the foaming of steelmaking slags, the weight of their physical properties has been investigated by comparing empirical equations of slag foamability with characteristic times of foam ageing. Looking for modelling it for the various compositions of slags, a machine learning model pre-trained in glasses and ceramics melts was validated for slag compositions. Based on its performance, a coupled framework with computational thermodynamics was proposed to predict the change in the characteristic times of foam ageing, an estimator of the foamability index. By applying this framework, alternative foam controller agents were investigated to replace a fluorine-based commercial solution in a steelmaking plant.

Naturally, further suggestions came along with the development of this project, which are summarised in the next section.

SUGGESTIONS FOR FUTURE WORK

- To expand the investigation on bubble generation for porous structures, i.e., accounting for the coalescence of bubbles during their growth and the roughness of the bubbler surface, the suggestion would be to conduct experimental investigations with porous structures of variable contact angle with water. These investigations would bring the results closer to the reality of steel ladles (and tundishes) where high contact angle compositions are applied to avoid metal infiltration;
- Also, looking for other compositions of purging plugs and measuring their contact angle with liquid metal could support the development of porous structures targeting bubble-induced flotation - mainly for the tundish, where a continuous injection of gas would control the infiltration of liquid metal, allowing lower contact angles to be feasible;
- Regarding the water model, although the current setup includes an overflow device, it only collects floated particles from the left side of the model, resulting in an accumulation of particles on the right side, near the water outlets. Thus, it is recommended to have a second apparatus on the right side, coupled with a procedure for constantly removing the floated particles from the top surface. In this matter, a constant injection of clean water or filtering the overflow back to the model would be initial ideas, requiring the calibration procedure to be revised;
- In addition to the removal efficiency results over time, it would be beneficial to obtain information about the particle size distribution as flotation progresses. To achieve this, the overflow device should be redesigned to facilitate the collection of particles and prevent their entrapment in the tubing. After sampling, the particles could be redispersed in ethanol and characterised using a particle size analyser (Malvern), thus avoiding the drying step;
- Considering the use of the machine learning model pre-trained in glasses and ceramic melts, as the training parameters are not optimised to also encompass slag compositions, a transfer learning approach would be recommended. In such a case, the pre-trained model on the large database of glasses is repurposed by training it on a smaller database of slags, adjusting its parameters.

- Having in mind the similarities between the empirical models of slag foamability and the characteristic times for foam ageing, a further investigation could look into how to optimise the coefficients and exponents to model slag foaming based on its physical properties. Also, the influence of each of the ageing mechanisms on this overall performance should be further investigated.

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