

Some Fundamental Aspects of the Dry Slag Granulation Process

Sharif Jahanshahi, Yuhua Pan and Dongsheng Xie*

CSIRO Minerals Down Under National Research Flagship, Clayton, Victoria, 3168, Australia

Abstract: There is a growing interest in development of a dry slag granulation (DSG) process so as to recover the sensible and latent heats from molten slags and convert iron blast furnace slags into a glassy phase that is a suitable replacement for Portland cement. The combination of waste heat recovery and conversion of slag into a saleable product could result in significant reductions in waste and emissions associated with production of steel and cement. The present paper covers some of the fundamental aspects of the reactions taking place during dry granulation of molten slag. In particular, the cut in sulphur emission from slag during DSG as compared with conventional wet granulation process and the dynamics of slag droplet collision with solid surfaces will be covered.

Published studies on the thermodynamics of sulphur in slags and the kinetics of sulphur transfer between blast furnace slags and oxidising gas mixtures have been reviewed to ascertain the effects of oxygen partial pressure on sulphur solubility in slags as well as the rate of desulphurisation by water vapor and oxygen containing gas mixtures at temperatures close to 1500 °C. Findings from these experimental studies show that the rate of removal of sulphur from slags could be considerably reduced by formation of sulphate or pyrosulphate species both within the slag as well as on the surface of the molten slag, and the desulphurisation of slags is considerably faster in Ar-H₂O than in Ar-O₂ with a high concentration of O₂.

New measurements have been made on the dynamics of wetting and the spreading of molten blast furnace slag droplets as they contact cold metal plates inclined at different angles. The observed behaviour follows a sequence of events (collision, spreading, recoiling, bouncing and/or rolling) which take place in tens of milli-seconds. The duration of the contact and the maximum spreading length were found to be strongly dependent on the initial size of the slag droplet and roughness of the steel surface. The maximum spreading lengths of the droplets were about three times the initial diameter of the droplets. The duration of the contact, spreading and recoiling was found to be strongly correlated with the size of the droplet. Over the temperature range of 1420 to 1580 °C, there was no significant effect of temperature on the dynamics of the wetting and spreading. Furthermore, it was found that droplets contacting the surface of an alumina plate exhibited a very different behaviour as compared with those contacting metal surfaces. In the case of alumina substrates the droplets had a larger maximum spreading diameter over a much shorter spreading period. Such wetting characteristics may be due to the slower heat transfer rate between the slag and the alumina substrate.

Keywords: molten slag, dry granulation, heat recovery, kinetics, sulphur transfer, dynamic wetting and spreading.

1. Introduction

Each year hundreds of millions tonnes of slags are produced as byproducts of ferrous and non-ferrous metallurgical industries worldwide. These molten slags contain vast quantities of thermal energy and are usually cooled with air or

water, thus all their sensible and latent heats (peta joules) are lost to the atmosphere. The air cooled slags form crystalline materials, which are either disposed of as waste in tailings dams or sometimes used as low value road based materials. The slags produced by the iron blast furnaces have high silica and lime contents and are increasingly processed using water quenching to form a glassy cementitious material that can be used to substitute for Portland cement. However, the conventional water granulation process consumes a large volume of fresh water through evaporation of 1000-1500 liters of water per tonne of slag. Given the growing pressure on our industry to reduce its wastes and emissions, there has been a growing need for new technologies that minimize the environmental impact of the industry. In the case of slags there is a need to capture and utilize the inherent values locked in molten slags while minimizing emissions and usage of fresh water.

The recovery of waste heat from molten slags through dry granulation has been the subject of numerous investigations with some successes being reported in the literature [1-9], however to date none of the proposed processes have passed the piloting or demonstration stages. In most cases air has been used as means of extracting the heat from the slag and the process has not gone beyond piloting stage. Two recent reviews [10,11] of alternative approaches to dry granulation of slags and heat recovery have shown some of the challenges involved and the current status of the technologies under development.

In Australia, CSIRO (Commonwealth Scientific and Industrial Research Organisation) has been working on the development of the dry granulation process since 2002 and has made some breakthroughs in process design to resolve the difficulties that have hindered previous attempts by researchers worldwide[10]. A novel disc design has been developed to produce fine granules without the formation of slag wool. A cyclonic air flow is employed to quench the hot granules to produce a highly glassy product with relatively low air input. These breakthroughs have made it possible to significantly reduce the droplet flying distance (hence a more compact granulator) and deliver a more efficient air quench process. This paves the way for recovery of the high-grade waste heat released from the slag.

In 2006, the Australian steel industry (BlueScope Steel and OneSteel) was engaged in this project and the conceptual process was proven through a series of tests using a purpose built and very compact prototype unit that dry granulated molten blast furnace slags and recovered the heat in form of hot air. The product was found to be more than 98% glassy and showed comparable cementitious properties with water granulated slags. Furthermore, it was demonstrated that sulphur emission from the slag could be suppressed through dry granulation with air, thus avoiding sulphur emission to the atmosphere through H₂S or acid mist, which could be a significant issue around water granulation plants.

The CSIRO's Dry Slag Granulation (DSG) process is as a continuous two-step process as shown in Figure 1. The molten slag is first atomized using a spinning disc and the fine droplets (< 2 mm) produced contact with flowing air and are cooled before colliding with the roof of the granulator and bouncing back before joining the cyclonic section of the reactor where further cooling and solidification take place. The hot granules then leave the first unit and enter a second unit (moving packed bed reactor) for further cooling to about 100 °C. Over 90% of the heat could be extracted via contact between the droplets/granulates and cold air. The remaining small fraction of the heat is transferred to the cooling water that is used to cool the spinning disc and the roof of the reactor.

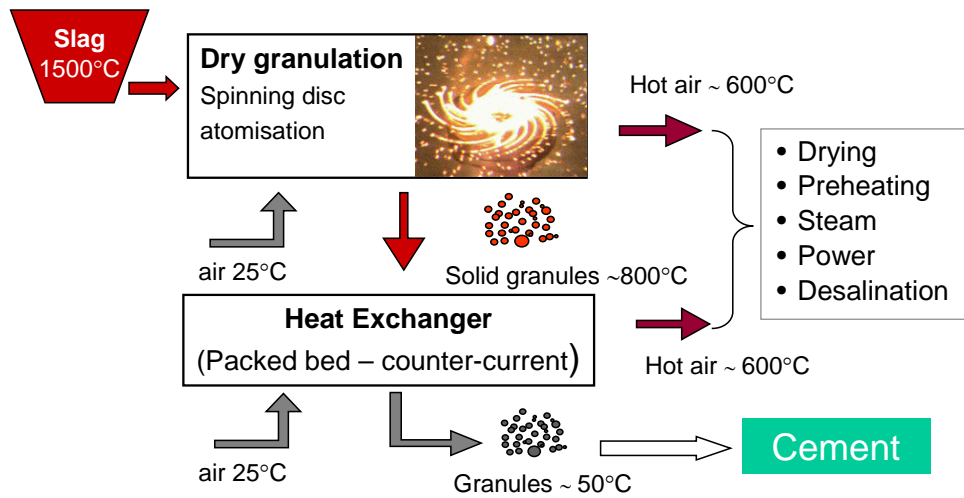


Figure 1: Conceptual process for integrated dry granulation and heat recovery, involving a granulator and a packed bed heat exchanger.

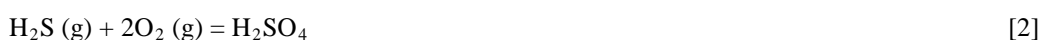
While the concept behind the process is simple, there have been a number of challenges involved in scaling up this process. However, with the development of sound fundamental understanding of the processes taking place inside the compact reactor we have been able to resolve the issues through developing sophisticated models of the process and using them for design of a semi-industrial scale pilot plant. This semi-industrial scale pilot plant is 3 metres in diameter and can granulate molten slags at about 6 t/h. This well instrumented unit has been constructed, commissioned and used for test work at CSIRO. The results obtained to date have been used to validate the in-house CFD (Computational Fluid Dynamic) models, which will be used for design of a full scale DSG plant at an industrial site.

It is beyond the scope of the present paper to cover various aspects and resolved issues with the development of the DSG process at CSIRO and the reader is referred to some of the recent publications by the present authors [10,12, 13]. For the audience of the MOLTEN12 conference, we are focusing on findings from a few fundamental studies that would be of general interest to “slag chemists”. These are:

- Thermodynamic and kinetic consideration of sulphur transfer between slag and gas during the granulation process.
- Wetting and spreading of molten droplets as they contact solid surfaces and their subsequent detachment.

2. Sulphur Transfer between Slag and Gas Phases

Sulphur emission during conventional water granulation is a significant issue. Chemical reactions such as:



could be responsible for the emission of sulphur bearing gaseous species, including acid mist. It is thus useful to examine the thermodynamics and kinetics of sulphur transfer under conditions of interest.

The thermodynamic behaviour of sulphur in slags has been extensively studied by numerous investigators and the effects of slag chemistry, oxygen potential and temperature have been quantified. In general, for a given sulphur

concentration in the slag, its activity is strongly dependent on slag chemistry, oxygen potential and temperature. At low oxygen pressures ($<10^{-6}$ atm), sulphur dissolves in the slag as sulphide (S^{2-}) species, while at high oxygen partial pressures ($>10^{-4}$ atm) sulphate (SO_4^{2-}) and/or pyrosulphate ($S_2O_7^{2-}$) species become stable [14-16] according to the following reactions:



For a given slag chemistry or basicity, the solubility of sulphur in slag will be strongly dependent on the oxygen partial pressure and temperature. At constant temperature, the sulphur solubility in slags decreases with increasing oxygen partial pressure until a critical oxygen partial pressure is reached where the sulphate species become equally stable. As the oxygen pressure is raised beyond this transition point of sulphide/sulphate, the solubility of sulphur in the slag increases. This behaviour is illustrated by the V-shaped curve in Figure 2.

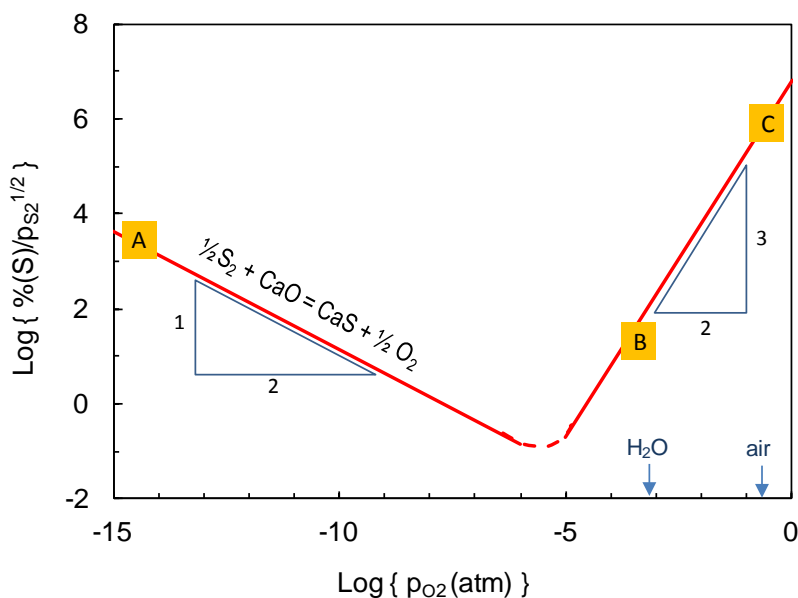


Figure 2: Estimated sulphur solubility $\{(\%S)/p_{S_2}^{1/2}\}$ in blast furnace type slag ($CaO-SiO_2-Al_2O_3$ with $CaO/SiO_2 \sim 1$) as a function of oxygen partial pressure (p_{O_2}) at 1500 °C based on the experimental data of Fincham and Richardson[14].

Under equilibrium conditions, the dissociation of water vapour results in an oxygen partial pressure of about 7×10^{-4} atm at 1500 °C [17]. Using Figure 2, one can see that when blast furnace type slags are reacted with water vapour at 1500 °C, the oxygen potential at the slag-steam interface could increase by several orders of magnitude to about 7×10^{-4} atm. According to Figure 2, this increase in oxygen potential will result in considerable (about two orders of magnitude) decrease in the sulphur solubility $\{(\%S)/p_{S_2}^{1/2}\}$ in the slag and hence transfer of sulphur from the slag to the gas phase becomes thermodynamically favourable. It is interesting to note that when the blast furnace slag contacts with air, rather than water/steam, the equilibrium oxygen potential at the interface raises to about 0.21 atm, where sulphate/pyrosulphate species become stable and consequently the sulphur solubility in the slag increases by about two orders of magnitude. It follows from the foregoing discussion that from thermodynamic point of view, blast furnace slag

granulation with water or steam is likely to result in the transfer of sulphur from slag to the gas phase, while dry granulation using air will minimise such transfer.

A number of investigators [18-21] have studied the kinetics of desulphurisation of blast furnace slags using Ar, Ar-O₂ and Ar-H₂O gases at temperatures up to 1550 °C. According to the findings of published studies on the kinetics of desulphurisation of blast furnace type slags, the effect of oxygen partial pressure on the stability of sulphide/sulphate also affects the kinetics of desulphurisation of the slag. As shown in Figure 3, Pelton, See and Elliott [18], found that at oxygen pressures of less than 0.03 atm, the desulphurisation rates are high and about $1\sim 2 \times 10^{-6}$ mol/cm²/s at 1415 °C. For the same slag and at same temperature, the rate drops by an order of magnitude to $0.9\sim 2 \times 10^{-7}$ mol/cm²/s at oxygen pressures of greater than 0.1 atm. This decrease in rate has been attributed to the poisoning of the surface by the formation of adsorbed oxy-sulphide species such as SO₄²⁻ at the interface, when Ar-O₂ gas mixtures were used for desulphurisation of slags. This interpretation is consistent with the measurements by Turkdogan and Pearce [20] on the rates of desulphurisation of slags with sulphide and sulphate species as well as the measured build up of sulphate species in blast furnace type slags by Mori et al. [21].

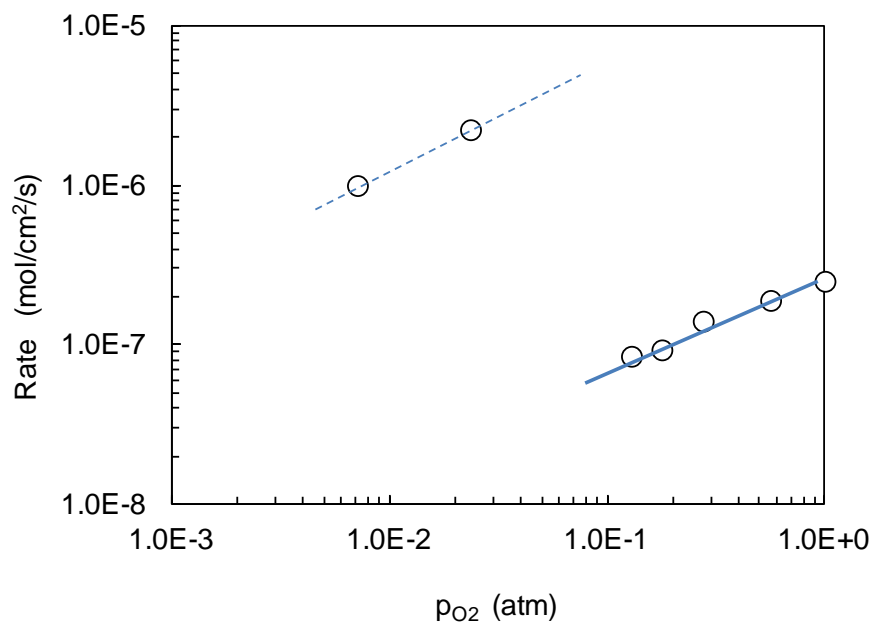


Figure 3: Effect of oxygen pressure on the desulphurisation rates of a blast furnace type slag at 1415 °C as measured by Pelton et al. [18], after Belton [22].

When Ar-H₂O mixtures were used, Agrawal, Yurek and Elliott [19] found that the desulphurisation rate increased linearly with p_{H₂O} at p_{H₂O} of greater than 0.1 atm. Extrapolation of their data to p_{H₂O} ~ 1 atm, gives values of about 5×10^{-7} mol/cm²/s at 1400 °C for slags containing about 1 wt% S. This is about a factor of 5 higher than the rates measured in Ar-O₂ mixtures with similar p_{O₂} as in air.

In a detailed review of published experimental data on desulphurization of blast furnace slags, Belton [22] had shown the kinetics of sulphur transfer are strongly affected by the presence of water vapor as well as oxygen partial pressure of

reacting gas and the sulphur content of the slag. The latter has been attributed to the effect of sulphur on lowering the surface tension of the slag and hence the active sites available for the gas-slag reactions to take place.

It follows that in oxidizing atmospheres, such as air, both the slag solubility for sulphur and the mechanism of sulphur transfer from slag to gas phase are expected to change due to formation of sulphate (SO_4^{2-}) species in the slag. These changes have marked effects on the rate of desulphurization of blast furnace type slags by a gas phase. Thus during dry granulation of blast furnace slags, the conditions are very favourable for suppressing the desulphurisation of the slag and hence one should be able to minimise sulphur emission. This has been demonstrated during our pilot scale dry granulation of blast furnace slags, where the slag samples taken before and after dry granulation did not show any measurable change in sulphur content as shown in Table 1. There was no smell of sulphur bearing gases during the dry granulation process. These findings show insignificant sulphur loss from the slag during the short period that the molten slag droplets are in contact with the air.

Table 1: Comparison of sulphur content in the slag before and after dry granulation.

Run #	wt % sulphur in slag	
	Dip sample taken before granulation	Granulated sample
16.1	0.52	0.52
17.1	0.65	0.68
17.9	0.73	0.72

3. Droplet Collision with Metal Plates

To develop an understanding of the mechanisms and governing parameters in the collision of molten slag droplets with solid surfaces, a series of droplet collision experiments was carried out under controlled laboratory conditions. In these experiments a high speed video camera was used to capture images of the collision sequence for analysis of the processes taking place as the molten droplets contact a cold steel plate, wet, spread and reform before rolling off or bouncing off from the plate.

A blast furnace slag containing about 42.1wt% CaO, 35.0% SiO_2 , 14.7Al₂O₃, 6.1MgO and 0.44 S was used. The slag had a liquidus temperature of about 1400 °C and most experiments were carried out between 1420 and 1580 °C.

The experimental apparatus used is shown in Figure 4. In each experiment 100-200 grams of the slag was placed in a graphite crucible, then heated and melted in a muffle furnace. The graphite crucible has a small orifice at the bottom with a stopper rod inserted in the orifice. After reaching the target temperature and homogenisation of the melt, the stopper rod was raised and discrete slag droplets were produced at the orifice, which fell freely under gravity till they contacted the solid steel plates. The high speed video camera recorded the collision of the droplet with the metal plate at speed of 1000 frames per second. Use was also made of crucibles with different orifice size to produce droplets with diameters in the range of 1 to 7 mm. The diameters of these droplets were measured from the video images of the droplets just before collision with the steel plate. The video images were subsequently analysed to quantify the effects of various parameters such as slag temperature, droplet size and velocity before contact, type and surface finish of plates used as well as the inclination angle of the plate.

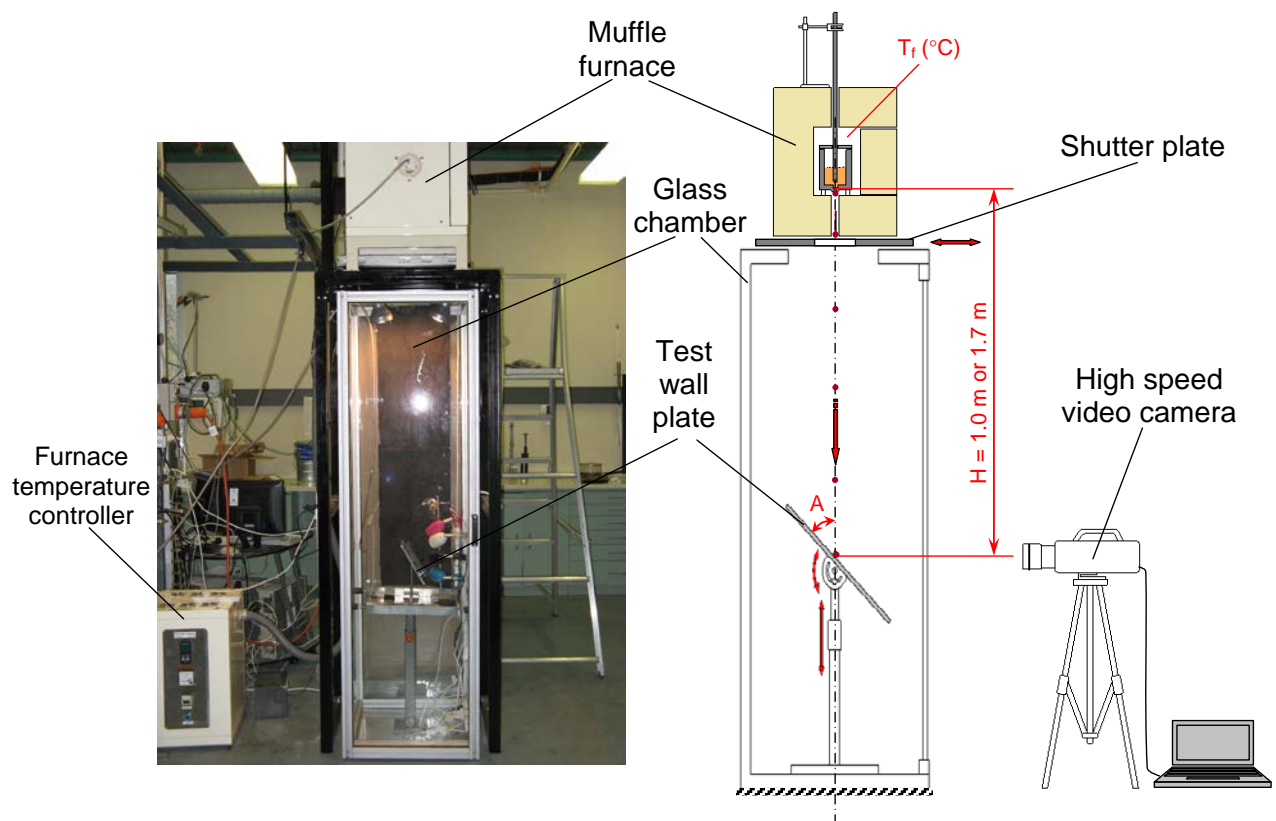


Figure 4: Experimental apparatus used for the droplet collision tests, where H is the free-fall height before collision, A is the inclination angle of the metal plate and T_f is furnace temperature.

Two types of experiments were conducted to study the effect of droplet velocity. In one type, the droplet free fall height was set at 1.0 or 1.7 metre above the inclined plate ($A = 15^\circ - 45^\circ$). These droplets had high velocities before collision. In the other type of experiment, the plate was kept horizontal and positioned much closer ($H = 0.3$ m) to the bottom of the crucible. These experiments focused on the droplet spreading on rather than colliding with the metal plate. The findings from these experiments are summarised below.

3.1 Droplet collision with inclined walls

Slag droplets with high velocities on collision with inclined surfaces generally exhibit a process of falling → contacting → spreading → recoiling → bouncing → rolling or tumbling, as shown in Figure 5.

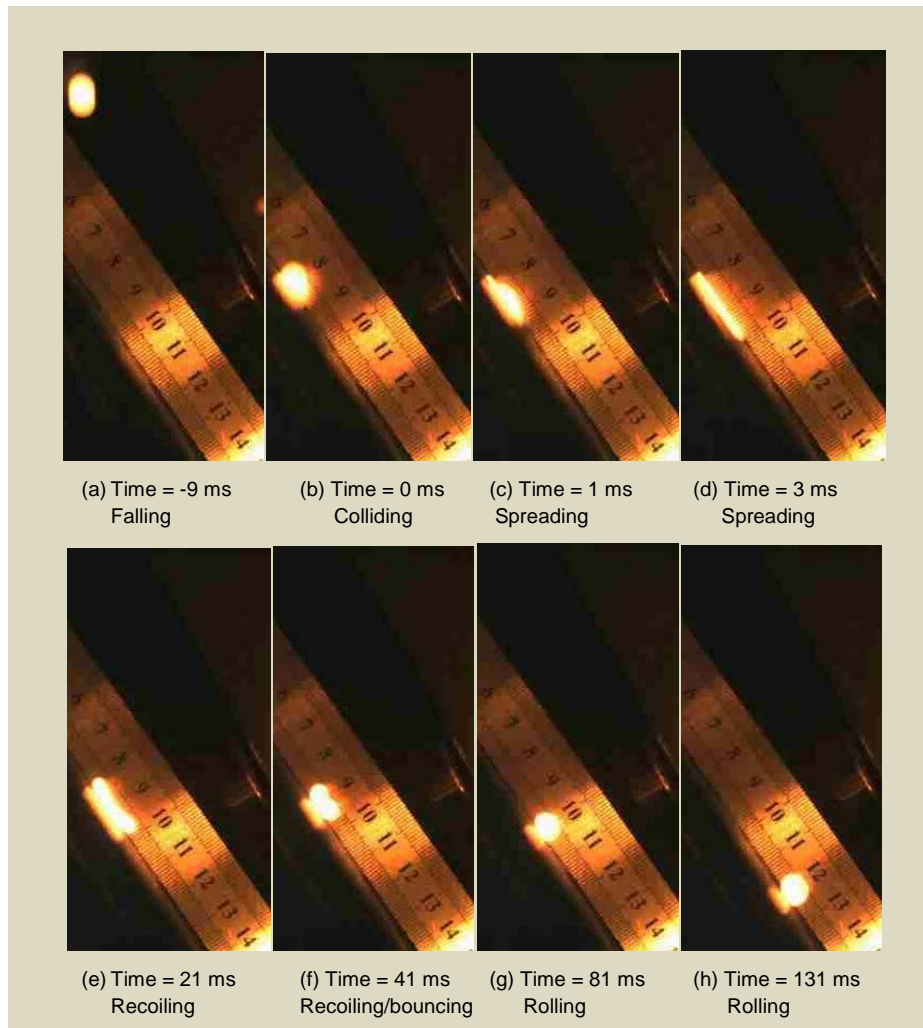


Figure 5: Sequence of still video images showing typical process of collision between a molten slag droplet and an inclined plate. Conditions: stainless steel plate, inclination angle $A = 30^\circ$, slag temperature $T_f = 1500^\circ\text{C}$, free-fall height $H = 1.7\text{ m}$.

The effects of droplet size on the maximum spreading length and spreading time are shown in Figure 6. These results were obtained from experiments carried out at 1500°C using a stainless steel plate inclined at 30° and placed about 1.7 m below the crucible bottom. It is evident that droplet size has significant effects on both the maximum spreading length as well as the spreading time before recoiling starts. These results show that larger droplets spread more and their spreading time could increase to about 50 ms before recoiling starts. The maximum spreading length is about 3 times the original droplet diameter.

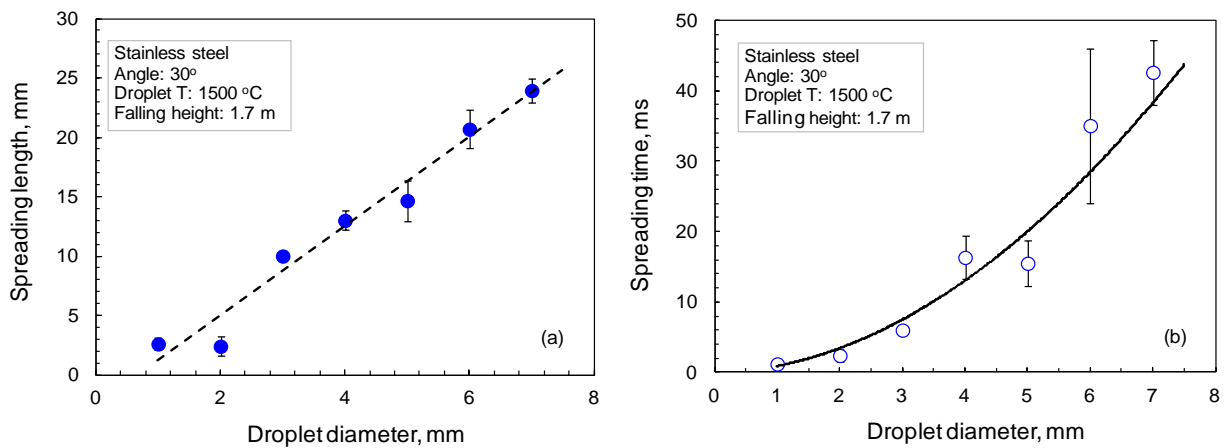


Figure 6: Effects of slag droplet size on: (a) maximum spreading length and (b) spreading time on an inclined ($A = 30^\circ$) stainless steel surface.

In Figure 7 the measured maximum spreading length and spreading time of the molten droplet during contact with a stainless steel plate inclined at 30° after a free-fall of 1.7 m are shown as a function of slag droplet temperature before collision. It is evident that that droplet temperature has a very mild effect, if any, on the maximum spreading length and spreading time.

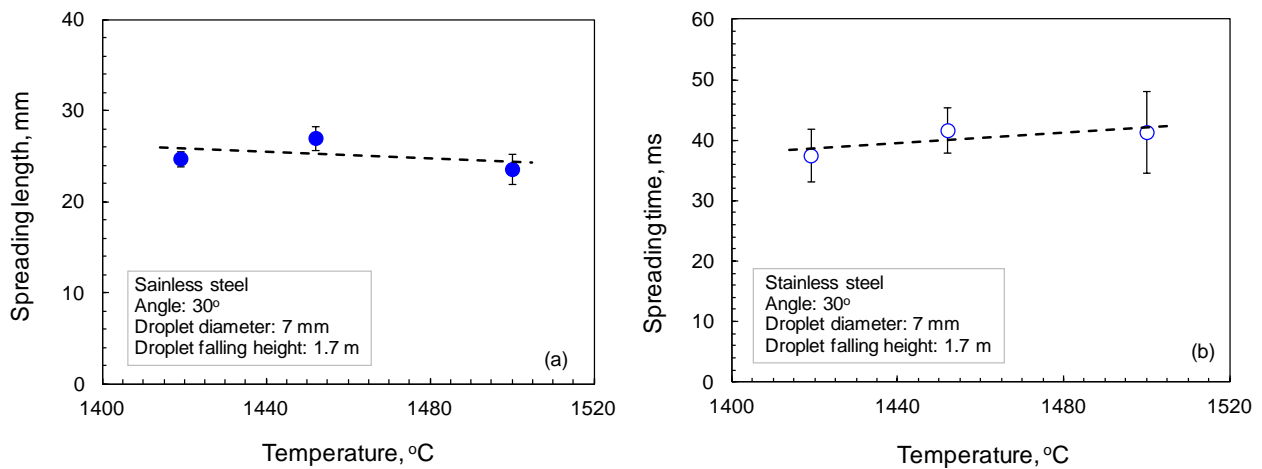


Figure 7: Effects of droplet temperature on: (a) maximum spreading length and (b) spreading time on an inclined ($A = 30^\circ$) stainless steel surface.

Droplets colliding on the stainless steel surfaces generally had slightly smaller maximum spreading lengths, but longer spreading times than on the mild steel surfaces (see Figure 8). This implies that the slag droplets seem more “sticky” to the stainless steel surfaces than to the mild steel surfaces.

With regard to the effect of the collision angle (A) defined in Figure 4, for a large droplet (7 mm in diameter), an increase in the collision angle led to a smaller maximum spreading length, but an increased spreading time. However, the magnitude of this effect decreased with the increase of the collision angle.

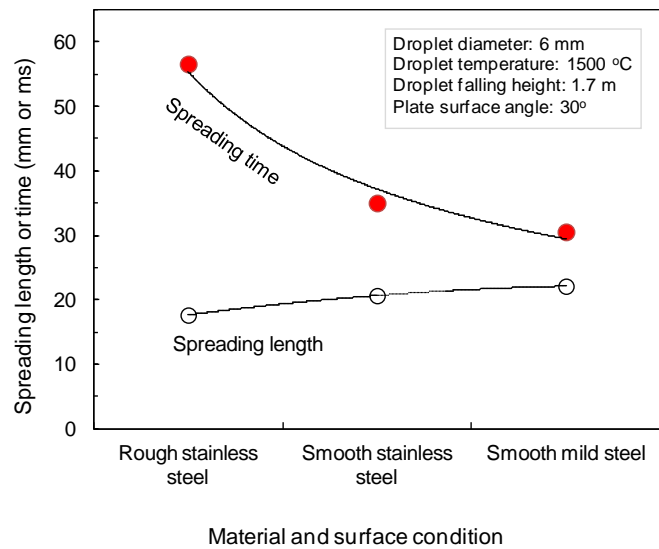


Figure 8: Effects of plate material and surface condition on maximum spreading length and spreading time of slag droplets colliding on inclined ($A = 30^\circ$) solid surfaces.

3.2 Slag droplet spreading at horizontal plates

The general sequence of events when molten slag droplets landed on horizontal plates after a short flight of about 30 cm in height could be summarized as: falling \rightarrow landing \rightarrow spreading \rightarrow recoiling \rightarrow bouncing, but without rolling or tumbling as compared with the droplet collision on inclined walls. These behaviours are shown in Figure 9. The total duration of events, i.e., from initial landing to bouncing, takes about 21 ms for droplets of about 5.7 mm in diameter. This duration increased with increasing droplet size as shown in Figure 10 (b), but seemed to be independent of the slag droplet temperature.

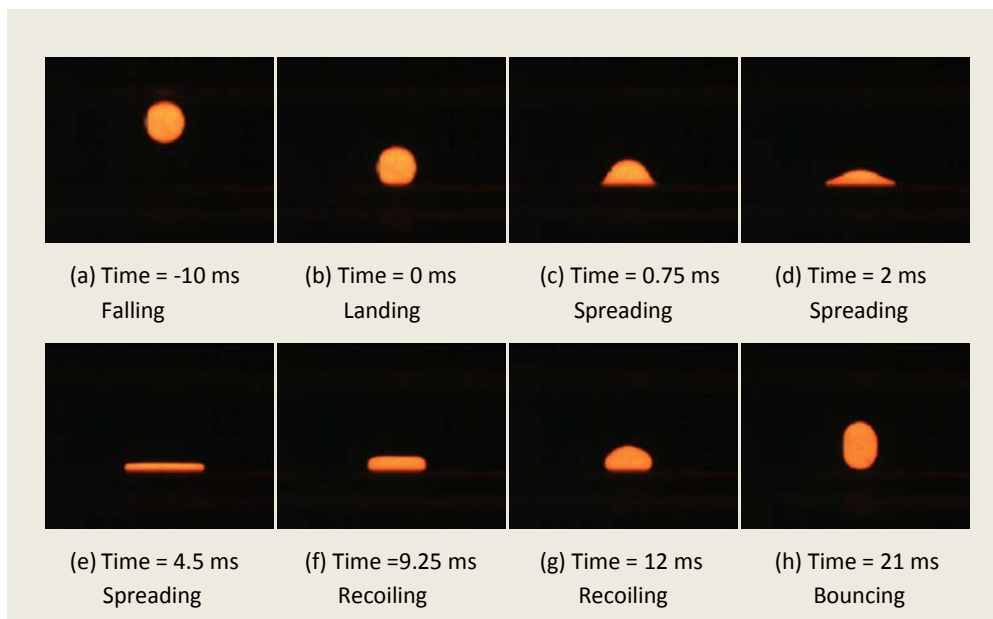


Figure 9: Sequence of still video images showing typical process of molten slag droplet spreading on a horizontal steel surface. Condition: Stainless steel plate at an angle (A) of 90° , molten slag temperature of 1500°C and slag droplet diameter of 5.7 mm.

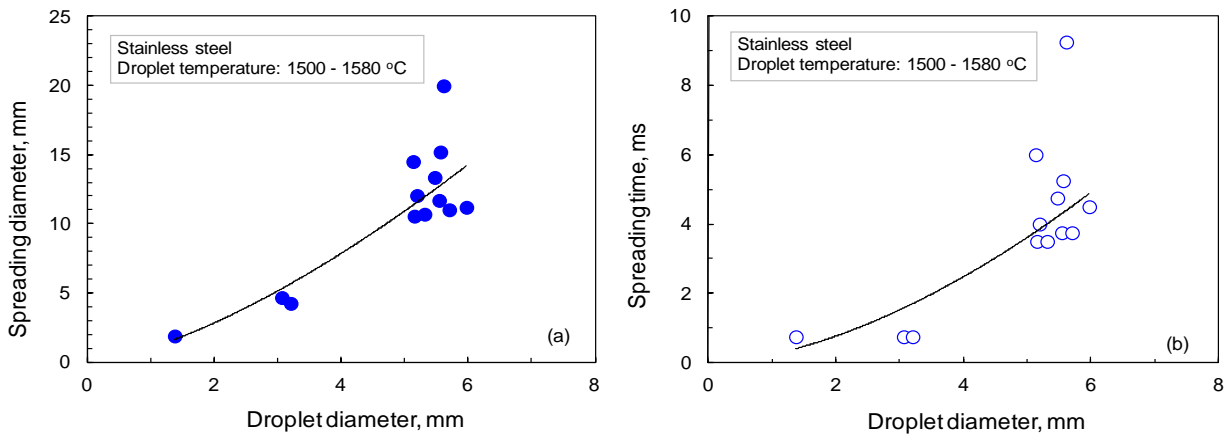


Figure 10: Effects of droplet size on: (a) maximum spreading diameter and (b) spreading time on a horizontal stainless steel surface ($A = 90^\circ$).

Measured effects of droplet size on maximum spreading diameter and spreading time are shown in Figures 10 (a) and 10 (b), respectively. These results show that larger droplets landing on the same type of solid steel surface result in larger maximum spreading diameters and longer spreading times for reaching the maximum spreading diameters, and vice versa. It is interesting to note that the spreading time for smaller droplets of less than 2 mm, is about 1 ms.

According to our results droplet temperature did not influence the droplet maximum spreading diameter and the spreading time, over the temperature range of 1500-1580 °C.

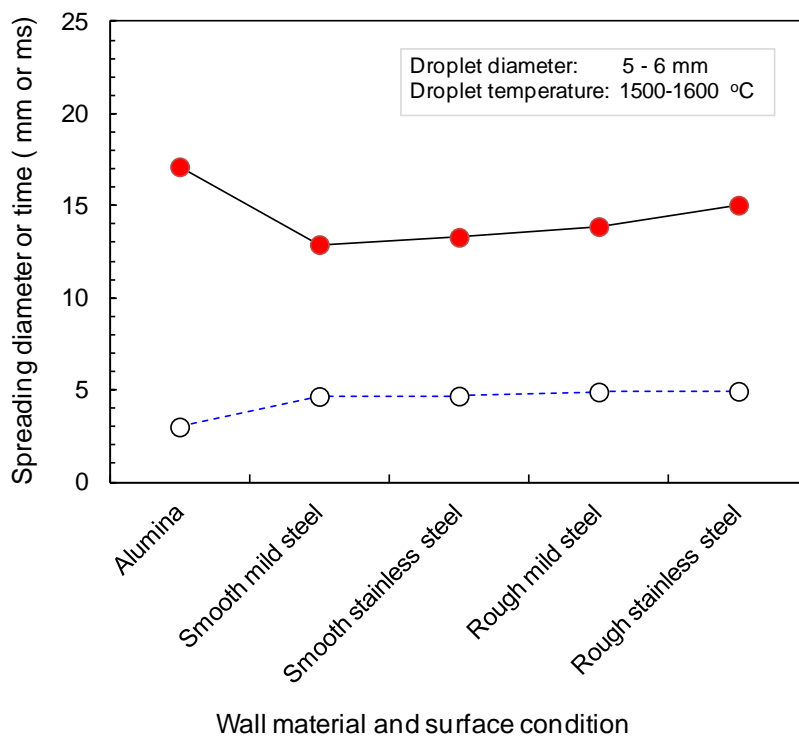


Figure 11: Effects of plate material and surface condition on maximum spreading diameter and spreading time of slag droplets landing on horizontal ($A = 90^\circ$) solid surfaces.

When different types of steel plates were used, as shown in Figure 11, it was found that droplets have similar maximum spreading diameters and spreading times on both stainless steel and mild steel surfaces. However, some differences were measured when the surfaces of the plates were polished or scratched. Rough surfaces tended to increase the maximum spreading diameters as well as the spreading times. Droplet spreading on an alumina surfaces exhibited a very different behaviour as compared with the metal surfaces. In the case of alumina substrates, the droplets had a large maximum spreading diameter, but a very short spreading time on the surface. This is thought to be due to the heat loss from the molten slag droplet to the alumina being relatively small thus droplets maintain sufficient fluidity to extensively and quickly spread and recoil.

Common to both the collision and the spreading experiments, for the same type of steel surface there is a strong correlation between the droplet maximum spreading extent (length or diameter) and the droplet spreading time for reaching the maximum spreading extent, showing that the larger the former the longer the latter.

These results, together with others made on different surfaces, require further analysis before a detailed model of the observed behaviour could be developed. In the meantime the results obtained have provided some useful data on the variations of contact time and area as droplets collide with steel surfaces (i.e., the roof and walls of the granulator). Such information has been used in our CFD model of the integrated process where heat transfer between molten slag droplets and cooling air and between the droplets and steel roof are estimated.

4. Conclusions

Published studies on the thermodynamics of sulphur in slags and the kinetics of sulphur transfer between blast furnace slags and oxidising gas mixtures have been reviewed to ascertain the effects of oxygen pressure on the sulphur solubility in slags and the rate of desulphurisation of blast furnace slags by water vapor and oxygen containing gas mixtures at temperatures close to 1500 °C. Findings from these experimental studies show that rate of removal of sulphur from slags could be considerably reduced by formation of sulphate or pyrosulphate species both within the slag as well as on the surface of the molten slag. The results also demonstrate that desulphurisation of slags is considerably faster when Ar-H₂O is used rather than Ar-O₂ with a high concentration of O₂.

Molten slag droplet collisions with metal plates have been studied under controlled experimental conditions. Droplet spreading and contact time during collision are significantly influenced by droplet size, wall materials selection and surface conditions/treatment. It was found that droplets colliding on the stainless steel surfaces generally spread less while in contact with the plate for longer time. Smooth surfaces will help to reduce the droplet spreading time.

Acknowledgement

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