Effect of Solidification and Cooling Methods on the Efficacy of Slag as a Feedstock for CO₂ Mineralization

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Iron and steel making (ISM) slag is often utilized to partially offset CO₂ emissions associated with metal production. Currently, the primary recycling method for slag is as β -Ca₂SiO₄ utilized in the cement industry, termed ground granulated blast furnace slag (ggbfs). However, the cement market is not large enough to exploit the entirety of ISM slag as ggbfs, relegating a large quantity of slag to reuse pathways with minor impacts on CO₂ reduction. Recent years have seen an increase in research into mineralizing CO₂ using the Ca and Mg content of ISM slags as a feedstock. Unfortunately, it has not been widely recognized that the solidification and cooling processes of slag dramatically effects its efficacy as a CO₂ mineralizing feedstock via modification of mineralogy, crystallinity, grain size, and micromorphology. This paper clarifies the key properties determining mineralization effectiveness and elucidates how to control these properties during the solidification and cooling process. The effect of solidification and cooling method on net CO₂ reduction is shown to be strongly dependent on solidification and cooling method along with the CO₂ intensity of energy generation.

KEY WORDS: slag; ironmaking; steelmaking; mineralization; CCUS; ggbfs; CO₂.

1. Introduction

The iron and steel making (ISM) industry contributes significantly to rising global greenhouse gas concentrations with the slag waste stream of ISM embodying a large quantity of CO₂ related to the calcination of (Ca,Mg)CO₃ and the heating of slag within the furnace. Efforts to offset the CO₂ associated with slag have occurred primarily via recycling slag to cement production (ggbfs)¹⁾ and more recently by integrating said process with the recovery of heat from slag.²⁾ Neglecting the energy to solidify, grind, dry, and transport ggbfs, the use of slag in cement production reduces CO₂ emissions by ~0.580 gCO₂/kg-ggbfs.³⁾ In comparison, 1 kilogram of Ca₂SiO₄ slag can potentially mineralization ~0.511 kg of CO₂ as CaCO₃ (again, neglecting operational energy). The superior CO₂ reduction of ggbfs is due to avoiding the fossil fuel combustion associated with the heating and decomposition of (Ca,Mg)CO₃ into (Ca,Mg)O and CO₂. In terms of CO₂ reduction, ggbfs is the current optimal reuse pathway for slag; however, the potential market size for ggbfs is on the order of 145 MT/y, while the production of BF slags is on the order of 272–327 MT/y.⁴⁾ There is an additional 145–218 MT/y of steel slag from BOF and EAF operations, the majority of which do not have the proper chemistry for utilization as ggbfs, regardless of market availability. Based on simple conversion of the Ca and Mg con-

tent, the ISM slag relegated to reuse outside of ggbfs contains ~103–150 MT/y of unexploited CO₂ capturing potential.

In recent years, research has focused on recovering heat from slags such that meaningful CO₂ reductions can be garnered from slag, regardless if it is to be recycled as ggbfs or not. In particular, the advancement of air-based heat recovery methods has increased the extraction of usable heat from slags. However, the potential CO₂ reduction gained via heat recovery is small when compared to the potential of slag to mineralize CO₂. Under idealized conditions,⁵⁾ the recovery of heat from slag instead of production by a current natural gas oven⁶⁾ would offset ~0.117 kgCO₂/kg-slag. Further, the application of air-based heat recovery to steel slags has technical and economic issues that remain to be solved.⁷⁾

CO₂ mineralization using the Ca and Mg content of ISM slags has received substantial research as conversion of (Ca,Mg)-silicates to (Ca,Mg)-carbonates is exothermic and slag is conveniently located adjacent to a concentrated CO₂ source. The theoretical CO₂ capture potential is dependent on the total (Ca,Mg) content of an ISM slag, and thus has significant variability from ~0.243–0.519 kgCO₂/kg-slag.^{8,9)} However, experimental difficulties related to slow reaction kinetics, the formation of passivating product layers (PL), and the trapping of mineral grains within unreactive species (mineral locking, ML) has substantially lowered the net CO₂ reduction provided by slag. To enhance the reaction kinetics researchers have explored a variety of mechanical, thermal, and chemical methods. There is a tendency in the field to assume the utilization of renewable energy directly

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for process operation and to ignore the CO₂ associated with chemical production; resulting in erroneously overstated net CO₂ reductions. However, the most effective use of renewable energy towards CO₂ reductions is as a direct replacement for CO₂-intensive energy sources.¹⁰⁾ Moreover, extant infrastructure and current investments into fossil fuel power sources implies that utility-scale energy will maintain a non-trivial CO₂ footprint at least until 2040.¹¹⁾ As the intent of slag-based CO₂ mineralization is to assist in reduction of global CO₂ emissions, it is mandatory to account for CO₂ associated with the energy and chemical consumption. When all sources of CO₂ are considered, the net CO₂ reduction of thermochemical slag-based CO₂ mineralization methods decreases substantially.¹²⁾ In this paper, the discussion is limited to slag-based CO₂ mineralization that occurs under atmospheric pressure, mild temperatures, and without chemical additives.

Despite decades of research, the majority of the literature either completely neglects or fails to adequately quantify the most fundamental characteristics of the slag that effect CO₂ mineralization: namely, mineralogy, crystallinity, grain size distribution (GSD), micromorphology, and the particle size distribution (PSD). The large variability in these characteristics introduces significant noise into experimental data; consequently, logically consistent trends about the effectiveness of operating parameters such as liquid-to-solid ratio, temperature, CO₂ partial pressure, and reaction time remain elusive.¹³⁾ Further, there is a failure to recognize that these traits are in large part controlled by the slag solidification and cooling processes employed at ISM facilities. This paper posits that slag-based CO₂ mineralization efficacy can be improved by control of the solidification- and cooling-dependent mineralogy, structure, and micromorphology of slags. In the next section, the dependence of slag-based CO₂ mineralization efficacy on slag mineralogy, crystallinity, GSD, micromorphology, and PSD are quantitatively discussed. Then, in section three, the control of these properties through the solidification and cooling process is elucidated. The net impact of solidification and cooling methods on slag-based CO₂ mineralization efficacy is quantified for prototypical iron slag and steel slag in section four.

2. Mechanisms Underlying CO₂ Mineralization Susceptibility of ISM Slag

2.1. Mineralogy and Crystallinity

In the slag-based CO₂ mineralization field, detailed study of the impact of mineralogy on mineralization efficacy is sparse. Despite studies highlighting the mineralogical variation between ISM facilities,¹⁴⁾ the typical reported information is limited to the slag source (*e.g.*, BF, BOF, EAF) and the elemental composition as simple oxides. Work from the silicate rock-based CO₂ mineralization field has shown that the ostensibly similar Mg₂SiO₄ and CaSiO₃ differ in CO₂ mineralization depth by ~4 orders of magnitude (≤ 40 nm¹⁶⁾ and ≥ 125 μ m,¹⁷⁾ respectively), despite comparable thermodynamic driving forces ($\Delta G_r = -34.7$ kJ/mol and -39.5 kJ/mol, respectively) and dissolution rates.¹⁸⁾ Though thermodynamics determines the initial surface reactions, the activation energy is structurally-dependent,¹⁹⁾ and the mineralogy determines the PL characteristics which are the pri-

mary inhibitory feedback on CO₂ mineralization reactions.

To quantitatively assess the importance of mineralogy in CO₂ mineralization, Bodor *et al.*²⁰⁾ and Ashraf and Olek²¹⁾ reacted synthetic minerals common to slag using autoclave reactors. These mild conditions are consistent with processes that may result in net CO₂ reduction and remove many of the complicating factors extant in more sophisticated reactor designs. Ashraf and Olek provided complete PSD graphs, allowing for accurate determination of reaction depth. Unfortunately, Bodor *et al.* did not adequately quantify the PSD. Because the powder generation methods were similar between the studies, the minimum and maximum PSD's from Ashraf and Olek's work were used to quantify the PL thickness in Bodor *et al.*'s work. The results, displayed in **Table 1**, indicate ~2 orders of magnitude variation in PL thickness between the minerals studied. Unfortunately, calcium aluminosilicate compounds, common to ironmaking slag, were not included in the studies.

2.2. Surface Area

Increasing the specific surface area (*i.e.*, the surface area per unit mass, SA) increases the overall reaction rate by limiting the passivating feedbacks of the PL and ML. The measured slag SA is sensitive to measurement method;²²⁾ at the μ m to mm scale the PSD and roundness are the primary features, at the nm to μ m scale surface roughness and porosity (ϕ) are the dominant features. The contribution of ϕ to SA is dependent on the average pore diameter (ϕ_D); equivalent ϕ with a smaller ϕ_D necessitates a longer total pore length and a larger potential SA due to the faster increase in volume over surface area for an expanding sphere. However, the theoretical potential SA does not mirror empirical results due to incomplete connectivity of pores. Empirical results and simulations suggest that pore length is limited to ~5 times ϕ_D .²³⁾ Porosity and ϕ_D are only sporadically reported in the slag literature; nevertheless, reported ϕ ranges from ~5 – 60% and the modal ϕ_D is reported to be 10 and 20 of nm. Taking into account that the effect of CO₂ mineralization is to smooth and round micromorphological features smaller than ~0.2 – 0.4 μ m²⁴⁾ while filling void spaces <0.15 μ m,²⁵⁾ the increase in SA of slag due to micromorphology is likely significant only during the initial reaction phase, after which the PSD is the sole feature with meaningful impact on SA.

Polettini *et al.*²⁶⁾ specifically evaluated the significance of particle size distribution (PSD) on slag-based CO₂ mineralization; their results confirm the basic geometric logic of increased SA promoting faster overall reaction rate and increased conversion. Despite its critical importance, PSD is not appropriately quantified in most papers. Due to non-gaussian size distributions that occur when grinding minerals at the micrometer-scale²⁷⁾ and the effect of grinding time on PSD,²⁸⁾ passing sieve size (D_{passing}), volume median diameter (D_{50}), surface area moment mean ($D[3,2]$), volume moment mean ($D[4,3]$), and other summary statistics are all insufficient to determine the reaction extent for a given reaction depth, or equivalently, the reaction depth given a conversion extent. Equation (1) applies the shrinking core model to reaction extent of a population of particles, where r_i is the radius of an individual particle, δ is the reaction depth, and n_i is the number of particles of radius r_i . **Figures**

Table 1. Gibbs energy of reaction, product layer depth, and specific comminution energy of some common slag minerals.

Mineral	Reaction depth (μm) [†]	SE_{IG} (J m/tonne)	SE_{GB} (J m/tonne)	SE_{IP} (J m/tonne)
MgO [‡]	1.322–7.594	34.485	30.918	27.352
CaO	–	22.417	19.855	17.293
FeO	–	8.580	7.718	6.857
Fe ₃ O ₄	–	10.599	9.349	8.100
MgFe ₂ O ₅	–	18.112	16.583	15.055
Ca ₂ Fe ₂ O ₅ [‡]	1.544–8.474	19.713	18.043	16.373
MgAl ₂ O ₄	–	35.175	31.825	28.474
Ca ₃ Al ₂ O ₆	–	30.873	28.174	25.475
Ca ₁₂ Al ₁₄ O ₃₃	–	36.523	33.388	30.254
Ca ₄ Al ₂ Fe ₂ O ₁₀	–	26.501	24.181	21.862
α -SiO ₂	NA	17.055	14.718	12.381
SiO ₂ ^a	NA	29.075	27.388	25.701
SiO ₂ ^b	NA	36.486	34.599	32.713
Mg ₂ SiO ₄	–	17.655	15.558	13.461
Mg ₂ Si ₂ O ₆	–	14.495	12.599	10.703
CaSiO ₃ ^{c, §}	0.197	20.192	17.771	15.351
CaSiO ₃ ^d	–	20.461	17.982	15.503
Ca ₃ Si ₂ O ₇ [§]	3.338	20.845	18.406	15.966
Ca ₂ MgSi ₂ O ₇ [‡]	0.631–4.319	18.031	15.771	13.511
β -Ca ₂ SiO ₄ [§]	≥ 7.202	14.993	13.005	11.018
γ -Ca ₂ SiO ₄ [§]	≥ 12.931	15.227	13.240	11.253
CaMgSiO ₄	–	16.388	14.342	12.296
Ca ₃ MgSi ₂ O ₈ [‡]	0.306–2.314	15.833	13.771	11.709
Ca ₇ MgSi ₄ O ₁₆ [‡]	1.544–8.474	12.153	10.441	8.729
CaFeSiO ₄	–	11.919	10.331	8.742
Ca ₃ SiO ₅ [§]	≥ 16.845	20.883	18.560	16.236
Fe ₂ SiO ₄	–	9.499	8.228	6.958
Mg ₃ Al ₂ Si ₃ O ₁₂	–	20.060	17.632	15.203
Ca ₃ Al ₂ Si ₃ O ₁₂	–	34.569	31.006	27.444
Ca ₂ Al ₂ SiO ₇	–	27.716	24.883	22.051
CaAl ₂ Si ₂ O ₈	–	23.459	20.691	17.924
Al ₂ SiO ₅	NA	34.121	30.958	27.796
Al ₆ Si ₂ O ₁₃	NA	28.212	25.192	22.173
CaCO ₃ ^e	NA	12.957	11.613	10.270
CaCO ₃ ^f	NA	8.561	7.777	6.994
CaCO ₃ ^g	NA	13.229	11.807	10.384
MgCO ₃	NA	16.286	14.728	13.170

[†] Reaction depth was calculated based on CO₂ mineralization extent and PSD using the shrinking core model. Bodor *et al.* did not include PSD information, so the range of PSD from Ashraf and Olek were used.

[‡] Data from Bodor *et al.*²⁰ Experimental conditions: incubator reactor, 30°C, atm. pres., 95% humidity, 20% CO₂

[§] Data from Ashraf and Olek.²¹ Experimental conditions: incubator reactor, 35°C, atm. pres., 94% humidity, 15% CO₂

a: Tridymite; b: Cristobalite; c: Pseudowollastonite; d: Wollastonite; e: Calcite; f: Aragonite; g: Vaterite

1(a) and 1(b) illustrate the effect of using summary statistics instead of the complete PSD on calculated reaction extent and reaction depth, respectively.

Conversion extent =

$$\sum_{r_i=r_{\min}}^{r_i=r_{\max}} \left\{ \left[\frac{r_i^3 - (r_i - \delta)^3}{r_i^3} \right] \times \left(\frac{\frac{4}{3} \pi r_i^3 n_i}{\sum_{r_i=r_{\min}}^{r_i=r_{\max}} \frac{4}{3} \pi r_i^3 n_i} \right) \right\} + \sum_{r_i < \delta} \left(\frac{\frac{4}{3} \pi r_i^3 n_i}{\sum_{r_i=r_{\min}}^{r_i=r_{\max}} \frac{4}{3} \pi r_i^3 n_i} \right) \quad \dots (1)$$

2.3. Mineral Locking

As is discussed in Section 3.1, when slag is solidified in a time frame of 10's of seconds to 10's of minutes (*e.g.*, water impingement, pit cooling), a large number of distinct minerals may concurrently nucleate and grow into one another. The ultimate effect is mineral locking (ML), the blocking of highly reactive species from taking part in CO₂ miner-

Fig. 1. Disparate results due to using summary statistics as opposed to the complete PSD when calculating reaction extent or reaction depth across a population of particles with the shrinking core model. Figure 1(a) plots the calculated conversion extent assuming an uniform reaction depth of 2 μm . Solid lines are the PSD represented as a cumulative volume distribution. Dashed lines are the cumulative reaction extent calculated using the entire PSD. The inset shows the effect of reaction depth when applied using the PSD with the shrinking core model. Figure 1(b) shows the calculated reaction depth for a population reaction extent of 75%. The PSD and summary statistics are those reported in Ashraf and Olek²¹ (black and orange data) and Santos *et al.*²⁹ (purple and green data). 'NR' indicates the data was not reported in the source papers. (Online version in color.)

alization by less reactive species. Probability and geometry dictate that the passivating effects of ML will increase as the number and variety of mineral grains increases. To quantify the effect of ML, a binary compound slag was simulated using a two-dimensional Voronoi cell-based Monte Carlo analysis (VCMC). The Voronoi cells are representative of nucleated grains and the simulation space is representative of a single slag grain. By altering the number of Voronoi cells (n_{VC}), the ratio (Ω) of the particle diameter to the average grain diameter (ϕ) was modified. In this way, the effect of grain size and grinding extent on ML was evaluated. Additionally, the concentration of the reactive species (c_R) was varied to assess effects on ML. The Voronoi cell-generating point coordinates were assigned via random number generator to mimic the stochastic nature of nucleation. ML extent was calculated as the area percentage of reactive species that did not directly contact the outer surface or were not connected via reactive cells to the outer surface. Each test condition (*i.e.*, Ω and c_R) was run 10 times or until the 90% confidence interval $< 5\%$, whichever was larger, to obtain estimates of population-level ML. **Figure 2(a)** displays the results of the VCMC and **Fig. 2(b)** displays several of the VCMC simulations for qualitative understanding. The results in agreement with intuition: namely, ML increases as Ω increases and as c_R decreases. Moreover, at high enough concentrations (*i.e.*, $c_R \approx 60\%$) the interconnectedness of grains essentially eliminates ML effects. As the VCMC is two dimensional and does not take into account ML that arises from the PL, these results should be considered as illustrative of the magnitude of the ML effect, but not neces-

sarily quantitatively accurate.

2.4. Grinding Energy

Aside from a few examples,^{12,30)} there is vanishingly little discussion of the energy required to grind slag to the 10's of μm used in most processes. When present, calculations of grinding energy are decidedly unsophisticated, limited to application of notoriously unreliable empirical fits (*e.g.*, Bond's Work Index) to minerals or scales not covered in the dataset. Grinding energy is dependent on material-specific parameters (*e.g.*, mineralogy, crystallinity, micromorphology, PSD) and equipment-specific parameters (*e.g.*, force application mechanism, energy loss to heat, noise, plastic deformation). Due to these complications, estimation of grinding energy across a wide range of minerals has historically eluded accurate computation. Tromans and Meech developed a first-principles calculation of the critical stress intensity for crack propagation and the accompanying energy release based solely on the microscale mineralogy and structure of the material.^{31,32)} Equation (2) calculates the minimum energy, equivalent to change in surface energy per unit mass (ΔSE , J/kg), required for the grinding a mass of particles of initial diameter (D_i , m) to a final diameter (D_f , m) based on material density (ρ , kg/m³), surface roughness (F_r , unitless), and surface energy (γ , J/m²). The surface roughness, F_r , is not expected to vary significantly between populations of particles, meaning the comminution energy is proportional to γ/ρ . The surface energy, γ , is dependent on the mineral in question, whether it is crystalline or amorphous, and whether the fracture is intragranular (IG), occurs at a grain boundary (GB), or is between disparate minerals ('interphase', IP). The surface energies, γ_{IG} and γ_{GB} , are one half the associated crack energy release (G_{IG} or G_{GB}) which are calculated via Eqs. (3) and (4), respectively. The interphase surface energy γ_{IP} is calculated equivalently to γ_{GB} but with modifications described below.

$$\Delta SE = \frac{6F_r\gamma}{\rho} \left(\frac{1}{D_f} - \frac{1}{D_i} \right) \dots\dots\dots (2)$$

$$G_{IG} = \left[\left(\frac{1-2\nu}{3} \right) \left(N^{2/3} M_\alpha \right) \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{R_0^{n-1}}{n \times R_x^n} - \frac{1}{R_x} \right) \right]_{R_x=R_0}^{R_x=R_{limit}} \dots\dots\dots (3)$$

$$G_{GB} = \left[\left(\frac{1-2\nu}{3} \right) \left(N^{2/3} M_\alpha \right) \left(\frac{e^2}{4\pi\epsilon_0} \right) \right] \times \left\{ \left[f \left(\frac{R_0^{n-1}}{n \times R_x^n} - \frac{1}{R_x} \right) \right]_{R_x=R_0}^{R_x=R_{limit}} + \left[(1-f) \left(\frac{R_0^{n-1}}{n \times R_x^n} - \frac{1}{R_x} \right) \right]_{R_x=mR_0}^{R_x=R_{limit}} \right\} \dots\dots\dots (4)$$

$$n = 1 + \frac{3ER_0^4}{(1-2\nu)M_\alpha} \left(\frac{4\pi\epsilon_0}{e^2} \right) \dots\dots\dots (5)$$

Poisson's ratio is denoted by ν , N is the atomic density of the unstrained crystal (1/m³), M_α is the combined Madelung constant ($= \alpha^2 M/a_n$; where α is the largest common valence on ions, M is the Madelung constant, and a_n is the stoichiometric number of atoms per molecule; unitless), e is

Fig. 2. The effect of ML as a function of the ratio (Ω) of particle size to grain size and the concentration (c_R) of reactive species (a) as calculated by 2D Voronoi cell-based Monte Carlo simulation. (b) Example Voronoi cell simulations showing the effects of increasing c_R and increasing Ω . (Online version in color.)

the elementary charge (1.602177×10^{-17} C), ϵ_0 is the permittivity in vacuum (8.854188×10^{-12} F/m), R_0 is the average distance between atoms in the unstrained crystal (m), R_x is the average distance between atoms in the x -direction due to a tensile stress in the x -direction (m), R_{limit} is equal to $R_0 + 2 \times 10^{-9}$ (m), f is the area fraction of grain boundary coincident sites ($=0.5$ for GB, $=0$ for IP), and m is a multiplying factor related to the distance between atoms at the grain boundary ($=1.5$ for GB and IP). The unitless parameter n is related to the bulk modulus of elasticity and is calculated using Eq. (5), where E is the equilibrium tensile elastic modulus (Pa).

The predictions of Tromans and Meech results in industrial comminution efficiency of $\sim 1\%$ when grinding to $40 \mu\text{m}$, consistent with the findings of empirical studies.²⁸⁾ Table 1 lists the material specific, theoretical minimum comminution energies of common compounds in fresh and carbonated slag as calculated by Eqs. (2)–(5). Material properties necessary for calculation were gleaned from the work of Vieillard³³⁾ and ‘The Materials Project’.³⁴⁾ The basic trend of fracture energy is $IG > GB > IP$, with $GB \approx 0.89$ IG and $IP \approx 0.88$ GB.

In homogeneously solidified slag (*i.e.*, amorphous structure), all fractures are IG as there are no grain boundaries. For amorphous solids a correction factor must be applied to account for the inherent ductility of the structurally disordered material. Comparison of the results of Wang *et al.*³⁵⁾ with Tromans and Meech indicate a consistent increase in fracture energy for silica, sodium silicate, and calcium aluminosilicate glasses over G_{IG} , G_{GB} , and G_{IP} of ~ 1.63 , ~ 1.78 , and ~ 1.96 , respectively; this covers the entire structural landscape of silicate glasses. These theoretical results are consistent with the result of Purwanto *et al.* which found fracture of RCA slag (amorphous) required ~ 1.82 times more energy than water-impinged slag (ostensibly a mixture of IG, GB, and IP fractures).³⁶⁾ In slags solidified moderately quickly (*e.g.*, water impinged, pit cooled), the polycrystalline structure results in the potential for IP, GB, and IG fractures. Though grain boundaries are plentiful, there is a random distribution in the alignment of grain boundaries to the application of force. This trait, combined with the short transgranular distance of polycrystalline slags, suggests a mix of IG, GB, and IP fractures will occur. In slowly solidified slag grains are much larger, resulting in IP and GB being the dominate fracture mechanism until exhausted. However, the GSD of such slags is typically larger than the necessary PSD for CO_2 mineralization, meaning IG grinding would be necessary for further size reduction.

Using the Eqs. (6)–(9) and the results from Table 1, general energetic guidelines for operating a slag-based CO_2 mineralization process can be derived for a given mineral considering the region-specific CO_2 intensity of energy generation. This paper focusses on mild operating conditions to obtain CO_2 mineralization, but does require a high concentration and purity CO_2 source. The CO_2 associated with separating and purifying CO_2 for mineralization is accounted for in Eq. (8).

$$\begin{aligned} \text{CO}_2 \text{ reduction} = & \dots (6) \\ \text{CO}_2 \text{ reduction potential} - \text{CO}_2 \text{ separation} - \text{Grinding} \end{aligned}$$

$$\text{CO}_2 \text{ reduction potential} = \left(\frac{\text{mol}_{\text{Ca}} + \text{mol}_{\text{Mg}}}{\text{kg}_{\text{mineral}}} \right) \left(\frac{\text{kg}_{\text{CO}_2}}{\text{mol}_{\text{CO}_2}} \right) \dots (7)$$

$$\text{CO}_2 \text{ separation} = \left(\frac{\text{kWh}}{\text{kg}_{\text{separated CO}_2}} \right) \left(\frac{\text{kg}_{\text{CO}_2, \text{released}}}{\text{kWh}_{\text{utility-scale generation}}} \right) \dots (8)$$

$$\begin{aligned} \text{Grinding} = SE \left(\frac{1}{D_f} - \frac{1}{D_i} \right) \dots (9) \\ (\text{equipment efficiency}) \left(\frac{\text{kg}_{\text{CO}_2, \text{released}}}{\text{kWh}_{\text{utility-scale generation}}} \right) \end{aligned}$$

The energy to separate and purify CO_2 from power plants was assumed to be 402 kJ/kgCO_2 .³⁷⁾ The current CO_2 intensity of energy generation for the major ISM regions is: China= 0.681 , OECD Asia= 0.561 , OECD Americas= 0.441 , and OECD Europe= $0.311 \text{ kgCO}_2/\text{kWh}$.⁶⁾ For polycrystalline slag, the mineral-specific grinding energy was assumed to be the average of IG, GB, and IP fractures. An equipment efficiency of 1% was assumed for all fractures. **Figure 3(a)** plots the net CO_2 reduction potential for several major slag minerals as a function of D_f . Figure 3(b) plots the net CO_2 reduction potential for $\beta\text{-Ca}_2\text{SiO}_4$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ in the four major ISM markets. These plots represent the depletion of CO_2 reduction potential due to supplying CO_2 and grinding energy, and do not take into account the aforementioned issues of ML and PL, nor is operation of ancillary equipment considered.

Fig. 3. Net CO_2 reduction potential vs. D_f (a) dependency on slag mineralogy and crystallinity, (b) dependency on the CO_2 intensity of energy generation in the major ISM regions. (Online version in color.)

3. Effects of Solidification and Cooling on Slag Characteristics

3.1. Solidification

Slag emerges from the ISM process as a molten melt, usually well above its compositionally-dependent liquidus temperature (T_L). As it cools, the formation of solid nuclei becomes thermodynamically favored as described by Eq. (10), where ΔG is the excess Gibbs Free Energy between the melt and nucleating solid, γ_s is the surface energy, L is the latent heat of fusion, T is the temperature, and θ is the contact angle between the nucleating solid and a surface. In the case of nucleation occurring in the bulk melt, θ is 180° and the third bracket reaches its maximum value of 1. This strong dependence of ΔG on the shape of a nucleating solid is reflected in the fact that the vast majority of ISM slag undergoes solidification instigated at boundaries with equipment (heterogeneous solidification). From Eq. (10), the driving force of solidification is dependent on the undercooling ($T_U = T_L - T$) of the melt. Likewise, the radius of a nucleating solid (r) that is stable against re-melting, and the steady-state nucleation rate (N) of said nuclei are temperature dependent, as shown in Eqs. (11) and (12).

$$\Delta G = \left(\frac{16\pi\gamma_s^3 T_L^2}{3L^2} \right) \left\{ \frac{1}{(T_L - T)^2} \right\} \left\{ \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} \right\} \quad (10)$$

$$r = \left(\frac{2\gamma_s T_L}{L} \right) \left(\frac{1}{T_L} \right) \quad (11)$$

$$N = f_0 C_0 \exp \left(\frac{-\Delta G}{kT} \right) \quad (12)$$

In Eq. (12), f_0 is the frequency of an atom attaching to the stable nuclei, C_0 is the number of atoms per unit volume, and k is the Boltzmann constant. The aggregation of molecules is a stochastic process and thus has an average lag time (τ) before an adequate number of molecules amass into a thermodynamically stable nucleus. The lag time, τ , is compositionally- and temperature-dependent. Equation (13) calculates τ per the method of Mokshin and Galimzyanov,³⁸⁾ where τ_g is the lag time at the glass transition temperature, $\tilde{T}_g$ is the normalized glass transition temperature, $\tilde{T}$ is the normalized temperature of interest, and ε is a dimensionless factor that accounts for the ability of a material to maintain structural disorder.

$$\tau = \tau_g \left(\frac{\tilde{T}_g}{\tilde{T}} \right)^\varepsilon \quad (13)$$

The dependence of mineralogy and GSD on T_U is complex. When slowly solidified (small T_U), nucleation events are rare, allowing for a nucleated mineral to grow through the melt without physical or chemical interactions from other growing minerals. As a result, a small number of simple oxides, with large grain sizes, are observed in slowly solidifying slags.³⁹⁾ Additionally, the large supply of thermal energy allows for restructuring of solids into thermodynamically favorable mineralogies and geometries. As T_U increases, the number of solid nuclei and the compo-

sitional variety of nucleating minerals increases. Minerals that are not compositionally-equivalent to the bulk melt alter the elemental composition of the adjacent melt as they grow. The local change in melt composition in turn alters the landscape of potential minerals that can nucleate;⁴⁰⁾ this phenomenon explains the small GSD, large variety of minerals, and high degree of ML that is observed in slags solidified under moderate T_U (e.g., pit cooling). When slag is homogeneously solidified, the local mineral composition is essentially isotropic and individual grains are absent.

For nucleation lag time, τ , the increase in ΔG due to increased undercooling (i.e., small to moderate T_U , or moderate to large T_U) is more substantial than the reduced kinetic energy concomitant with temperature decrease, resulting in a decrease in τ . However, as T_U increases the kinetic barrier eventually prevents the arrangement of molecules into thermodynamically-favorable geometries, delaying solidification until the entire melt becomes thermodynamically predisposed to solidify. This ‘homogeneous’ solidification generates a solid slag without long range atomic order, so-called ‘amorphous’ or ‘glassy’ slag. The large T_U required for homogeneous solidification also drives heat transfer, which in turn reduces the T_U . Due to this feedback, homogeneous solidification is only successfully applied to small slag volume such as the <2 mm diameter particles produced in the rotary cup atomization method (RCA).⁴¹⁾ Examination of water-impinged slag indicates it is not truly amorphous,³⁹⁾ but rather polycrystalline with grain sizes on the order of a few micrometers; nevertheless, the rapid cooling suppresses the transition of β -Ca₂SiO₄ to γ -Ca₂SiO₄, making water-impinged slags suitable for use as ggbs.

In addition to mineralogy and GSD, the ϕ of slag is affected by the solidification conditions. Rapid solidification methods involving water tend to result in very high ϕ slags regardless of the process details,⁴²⁾ whereas the ϕ in air cooled slags is sensitive to the equipment.⁴³⁾ The porosity, ϕ , is dictated by the exclusion of gas from the solid phase upon phase transition from liquid to solid, followed by nucleation of gas pores, Ostwald ripening of the pores, and growth along grain boundaries when present. In general, longer solidification times lead to larger ϕ_D , longer pore networks, and lower pore network tortuosity.

3.2. Cooling

The high solidus temperature of ISM slags imbues solid slag with substantial thermal energy that can potentially alter its structure and micromorphology. The thermal energy content of Ca₂SiO₄ from 1 300 K to 300 K is ~316 kJ/kg.⁴⁴⁾ For slag cooled via natural convection (e.g., pit cooling), this inherent thermal energy is sufficient to restructure β -Ca₂SiO₄ to γ -Ca₂SiO₄.⁴⁵⁾ More rapid cooling, as occurs in heat recovery and quenching methods, prevents this phase transition.⁴⁶⁾

The mineralogy, structure, and micromorphology set by the solidification process controls what micromorphological changes are possible during cooling. In homogeneously solidified slag, the thermophysical properties are isotropic and, owing to the amorphous structure, generally resistant to thermal restructuring into crystalline structures⁴⁷⁾ or thermally-induced fracturing.⁴⁸⁾ When slag is solidified more slowly, the appearance of distinct, mineral grains means that

structural (e.g., β - to γ -Ca₂SiO₄ phase transition) and micro-morphological (e.g., micro-scale fracturing) alterations are possible. Phase transition requires slow cooling such that sufficient time and energy is available for structural rearrangement of atoms. On the other hand, micro-scale fracturing requires rapid cooling such that large thermal gradients exist between adjacent portions of the slag. The thermal stress (σ_t) within slag is given by Eq. (14), where ΔT is the temperature difference, α is the linear coefficient of thermal expansion, E is Young's modulus, λ is the relaxation time, and K is the relaxation parameter. Due to differences in thermal conductivity (κ) and α , thermally-induced stresses are particularly large at the grain boundaries of distinct minerals. In previous work, the authors demonstrated that quenching of high temperature, solid slag can generate fractures throughout a polycrystalline Ca₂SiO₄ network, especially at boundaries between disparate minerals.⁴⁹⁾ According to simulations mimicking the experimental conditions (i.e., 1 173 K, 3.6 mm diameter Ca₂SiO₄ quenched in 293 K water), the energy available to induce fractures in slag was ~88 J/g, slag, after accounting for energy transfer to heat and vaporize water, and the fact that thermal stress exceeded fracture stress only during the first few milliseconds of quenching. This rapid moderation of thermal stresses with quenching explains why water-impingement of molten slag fails to generate large quantities of microfractures.

$$\sigma_t = \Delta T \alpha E e^{\left(\frac{-\lambda E}{K}\right)} \dots \dots \dots (14)$$

4. Theoretical Effect of Solidification and Cooling on Slag-based CO₂ Mineralization Efficiency

Estimation of the magnitude of the effect of the solidification and cooling processes on the net CO₂ reduction of

slag-based CO₂ mineralization was performed. The analysis was confined to industry average ironmaking and steelmaking slag compositions.¹⁵⁾ Solidification conditions were grouped into homogeneous (e.g., RCA), large T_U (e.g., water impingement), moderate T_U (e.g., pit cooling), and small T_U (c.f. Gautier *et al.*). Cooling time from solidus temperature to ambient temperature was set as seconds (quench), minutes (heat recovery), and hours (natural cooling). The mineralogical composition for steel slags was based on the work of Gautier *et al.*³⁹⁾ and extended to iron slags using assumptions based on the underlying physical mechanisms as discussed in this paper. The effects of quenching on micromorphology were based on previously published work.⁴⁹⁾ Due to a lack of empirical data, ϕ was not considered. The final grind diameter, D_f , was set such that complete conversion of Ca and Mg to carbonates was assured. The grain size (ϕ) and concentration for each mineral was used to determine the D_f range necessary to keep ML to < 5% using the results summarized in Fig. 2(a). The D_f range was separately calculated as twice the mineral-specific reaction depth. The D_f range with the smaller values was set as the D_f range for all minerals within the slag. When $\phi > D_f$, the ϕ was used to set the diameter at which a change in fracture mechanism occurs (D_m) for each mineral. The grinding energy for each condition was calculated using Eq. (9) with the mineral specific grinding energy from Table 1. Given the range of values for ϕ , D_i , D_m , and D_f , a Monte Carlo analysis was performed to determine the overall fracture energy for each solidification and cooling condition. Each condition was run 5 000 times, with a normal distribution being produced from the values listed for each of the parameters in Table 2. The values listed represent the 10th and 90th percentile when generating the normal distributions, but were also used as the limiting values for calculating the minimum and maximum potential grinding energy, in order to filter outlier results

Table 2. Conditions and values used in the analysis of the effect of solidification and cooling methods on iron and steel slag-based CO₂ mineralization efficiency. Estimated comminution energy to achieve full conversion of each slag under the given solidification and cooling conditions is also shown.

	Solidification type	Cooling type	Assumed mineralogy	D_i (μm)	D_m (μm)	ϕ min (μm)	D_f (μm)	Fracture mechanism	Grinding energy mean, median (kJ/kg)
Steelmaking slag	Homogeneous	Heat recovery	Amorphous {Ca ₂ Fe ₂ O ₅ –CaSiO ₃ } (100%)	800–2 000	NA	NA	0.4–16.9	IG with correction factor	5 763, 3 698
	Large T_U	Heat recovery	β -Ca ₂ SiO ₄ (50%), Ca ₂ Fe ₂ O ₅ (50%)	3 000–5 000	NA	2	2.8–13.8	$\overline{\text{IG, GB, IP}} (D_i \rightarrow D_f)$	2 175, 1 953
	Moderate T_U	Quench	Silicates (50%), Ca ₂ Fe ₂ O ₅ (20%), CaO (15%), MgFe ₂ O ₅ (15%)	5 000–10 000	33–67	5	6.2–13.2	$\overline{\text{IG, GB, IP}} (D_i \rightarrow D_m)$,	2 018, 1 939
		Heat recovery Natural						IG ($D_m \rightarrow D_f$)	2 020, 1 940 2 020, 1 940
	Small T_U	Quench	Ca ₂ SiO ₄ (50%), Ca ₂ Fe ₂ O ₅ (45%), MgO (5%)	3 600	95–185, 124–224, 41–89	20	2.6–15.2	IG ($D_m \rightarrow D_f$)	1 648, 1 500
		Heat recovery Natural						IP ($D_i \rightarrow D_m$), IG ($D_m \rightarrow D_f$) IP ($D_i \rightarrow D_m$), IG ($D_m \rightarrow D_f$)	2 266, 2 137 2 153, 1 943
Ironmaking slag	Homogeneous	Heat recovery	Amorphous {Ca ₂ Al ₂ SiO ₇ –CaSiO ₃ } (100%)	800–2 000	NA	NA	0.4–16.9	IG with correction factor	6 788, 4 319
	Large T_U	Heat recovery	Silicates (76%), Aluminosilicates (24%)	3 000–5 000	NA	2	2.8–13.8	$\overline{\text{IG, GB, IP}} (D_i \rightarrow D_f)$	2 599, 2 333
	Moderate T_U	Quench	Silicates (76%), Aluminosilicates (24%)	5 000–10 000	33–67	5	6.2–13.2	$\overline{\text{IG, GB, IP}} (D_i \rightarrow D_m)$	2 184, 2 081
		Heat recovery Natural						IG ($D_m \rightarrow D_f$)	2 185, 2 083 2 189, 2 079
	Small T_U	Quench	Ca ₂ SiO ₄ (60%), Aluminates (40%)	3 600	95–185, 124–224	20	3.1–16.9	IG ($D_m \rightarrow D_f$)	2 007, 1 799
		Heat recovery Natural						IP ($D_i \rightarrow D_m$), IG ($D_m \rightarrow D_f$) IP ($D_i \rightarrow D_m$), IG ($D_m \rightarrow D_f$)	2 313, 2 097 2 403, 2 161

from the Monte Carlo analysis. The average and median values from the Monte Carlo analysis for each condition are provided in Table 2. Histograms of each solidification and cooling condition with bins set at 50 J/kg are provided in Fig. 4. The results from the Monte Carlo analysis were used to calculate the net CO₂ reduction for each solidification and cooling scheme in China and Europe using Eqs. (6)–(9). The results are summarized in Fig. 5.

Figures 4 and 5 indicate that homogeneous solidification methods may severely diminish the net CO₂ reduction of slags used for CO₂ mineralization. This effect is enhanced in areas where the CO₂ intensity of energy production is high. The precision of the predicted CO₂ reduction for homogeneously solidified slag could be improved by empirically determining the PL depth of such slag under mild mineralization conditions. Figures 4 and 5 indicate that quenched, small T_U -solidified slag provides the greatest CO₂ reduction. The large GSD of small T_U slag makes the generation of microfractures via quenching especially efficient, reducing the required grinding energy. The variation in grinding

energy and net CO₂ mineralization is minimal for all other solidification and cooling methods. Large variation in net CO₂ reduction is seen between ironmaking and steelmaking slag. The use of industry average slag compositions conceals the intra-industry mineralogical variation, in turn producing grinding energy and CO₂ reduction ranges that may be reasonable for a single facility, but are too constrained for the ISM industry as a whole. Small T_U solidification methods should largely counteract the compositional variations as the thermodynamically-preferred species show minimal variation at the level of compositional variation observed between ISM facilities using equivalent equipment and methods. The local CO₂ intensity of energy generation remains the strongest influence on slag-based CO₂ mineralization efficacy. This trend should hold for all CO₂ mineralization technologies, thus highlighting the importance of countries moving to lower CO₂ intensity energy sources.

5. Conclusions

In this work, the properties of ironmaking and steelmaking slag (*i.e.*, mineralogy, crystallinity, GSD, micromorphology, and PSD) were shown to have a significant effect on its behavior under CO₂ mineralization conditions (*i.e.*, grinding energy, mineral locking, product layer depth). It was further demonstrated that the slag properties are sensitive to the solidification and cooling conditions applied to molten slag. These magnitude of these effects was quantified over the range of solidification and cooling conditions typical to ISM processes. It was shown that the factors effecting net CO₂ reduction of slag-based CO₂ mineralization follow the general trend of CO₂-intensity of energy > slag mineralogy > solidification and cooling method. It was noted that slag mineralogy is determined by solidification and cooling method, highlighting its central importance.

A slow solidification method (small T_U), coupled with quenching the hot, solid slag was shown to produce the largest net CO₂ reduction. It was noted that this method also circumvents the issue of compositional variation of slag. Homogeneous solidification methods (*e.g.*, RCA) were shown to dramatically increase grinding energy, suggesting abundant caution in their use is prudent if they are to be used for CO₂ mineralization or as ggbs. Studies into the PL depth of homogeneously solidified slag to provide more accurate analysis of D_f are warranted.

All solidification and cooling conditions provided net CO₂ reductions from ISM slag without the use of chemical additives or extreme temperatures and pressures. These results suggest current technology and techniques are sufficient to begin reducing the CO₂ intensity of ISM through slag-based CO₂ mineralization. It seems reasonable to suggest that research efforts should be switched from exploring energy-intensive thermochemical CO₂ mineralization pathways to controlling the slag properties at the point of production at the ISM facility. For all methods this paper highlighted the importance of properly quantifying the properties of slag used in experiments; of primary importance are supplying the complete PSD, the GSD, and the mineralogical composition.

Several niche areas of slag-based CO₂ mineralization deserve more attention based on these results of this paper.

Fig. 4. Histograms of the energy intensity of grinding iron and steel slags to achieve complete conversion of Ca and Mg to carbonates according to Monte Carlo simulation (5 000 runs per condition). Bins are set at every 50 J/kg. (Online version in color.)

Fig. 5. Net CO₂ reduction of iron and steel slag-based CO₂ mineralization in China and Europe based on solidification and cooling conditions. Boxes show median, lower and upper quartile; whiskers show 5% and 95% values. (Online version in color.)

The quantification and control of slag porosity can potentially increase the specific surface area significantly, but feedbacks with mineralization reactions and dependence on solidification techniques makes this difficult to quantify at present. Slag abrasion concurrent to CO₂ mineralization may greatly reduce the grinding energy due to the lower specific grinding energy of carbonates (Table 1), the lower energy of the interphase bonds inherent to the product layer, and the smaller surface area required per abrasive event compared to fracture events. Additionally, abrasion concurrent to CO₂ mineralization would counteract the passivating effects of the product layer.

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