修 士 論 文 概 要 書

Summary of Master's Thesis

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研究題目 Title	Reducing the Carbon Footprint of the Iron and Steel Making Industry ~Separation and Conversion of Constituent Elements of Slag~				

1. Research Purpose

The Iron and Steel Making (ISM) industry accounts for 43% of Japan's CO_2 emissions despite being a world leader in efficiency. In an effort to further reduce ISM's carbon footprint, the reclamation and utilization of high exergy materials (Fe, CaO) within the major waste stream of the industry (slag) was studied. The primary barrier to this is the dispersed, μm-sized nature of the useful compounds. Traditional recovery methods require grinding of slag to 10's of μm, the energy requirements of which diminishes the overall CO_2 reduction. In this study, two methods were applied to increase material recovery while reducing energy expenditure: 1) quenching high-temperature, solid slag to induce fractures and reduce grinding energy, and 2) separation of molten slag into pure layers using a centrifuge.

2. Research Method

Desilication slag received from an ISM company was used for testing and as a model by which to build and check simulations. From analysis of the slag and an extensive literature review, ISM slag can be separated into Silica (SiO_2 matrix with Fe^0 inclusions), Calcium Silicate (Ca_2SiO_4 matrix with Fe_XO_Y inclusions), and Calcium Ferrite (homogeneous $Ca_2Fe_2O_5$) type slags.

2.1. Quench Experiments

SiO_2 and Ca_2SiO_4 slag was heated to 900 ˚C in an electric furnace and subsequently quenched in 20 ˚C water or cooled via natural convection in room air. The slag samples were then crushed and the comminution energy was measured. An additional control group (no heat treatment) was also crushed. Tests were carried out on three sizes groups (Ø=3.6±0.6, 7.8±1.8, and 13.5±2.4 mm), with each test condition being comprised of at least 30 samples. $Ca_2Fe_2O_5$ slag was not tested because no free Fe is present in the structure.

2.2. Quench Simulation

The conditions of the slag quenching were built into a 2D heat transfer and thermal-stress analysis using COMSOL Multiphysics®. The size distribution of void spaces and Fe^0/Fe_XO_Y inclusions were based on examination of the slag. The boundary layer condition for quenching in water took into account film boiling. Thermal stress levels above the fracture stress of the slag matrix were assumed to cause fractures. Reduction in grinding energy was calculated as the volume of slag that incurred fractures.

2.3. Molten Separation Experiments

The potential for molten separation of slag was tested by inspecting the desilication slag for evidence of density-based separation. Samples were analyzed using XRF to determine the elemental composition and compared.

The potential for remixing of centrifuged slag upon deceleration was tested using a rectangular, 2D container filled with two liquids layers of different densities. Rotation of the apparatus mimics the deceleration-induced movement of liquid layers and the potential for remixing via Kelvin Helmholtz Instability (KHI).

2.4. Molten Separation Simulations

A program was written in Fortran to calculate the transient composition of centrifuged slag, heat loss, and the energy required to operate the centrifuge. The centrifuge length to diameter ratio (L/D) and angular velocity were varied to determine the optimal operational scheme. The transient composition and temperature of slag was used to analyze the potential for premature solidification.

The potential for KHI remixing upon deceleration was analyzed by converting the classical theory to account for centrifugal force and by applying a correction factor to account for the effects of walls (based on testing and literature review).

3. Research Results

3.1. The effect of thermal-shock on grinding energy

Figure 1 shows the aggregated results of testing and simulation. Simulations and experiments were in agreement in all cases, leading credence to the concept of slag quenching. SiO_2 slag does not fracture from quenching, but the boundary between SiO_2 and Fe^0 inclusions fracture due to significant differences in response to quenching. Fracturing occurs in Ca_2SiO_4 slag due to quenching, but preferential fractures do not occur at boundaries with Fe_XO_Y inclusions. Reduced distance from the heat transfer surface to the center of slag leads to greater reductions in grinding energy due to more thorough penetration of thermal stress.

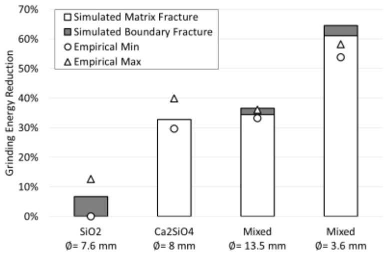

Figure 1: Experimental and Simulation Results of Slag Quenching

Application of the quenching process involves allowing slag to slowly cool until solid (to increase crystallinity and heat transfer rate), followed by quenching, separation of $Ca_2Fe_2O_5$, and grinding for Fe recovery. If applied to all Japanese ISM slag (recovered Fe → Electric Arc Furnace; recovered Ca_2SiO_4 → concrete production) CO_2 emissions would be reduced by 12 Mtonne/year.

3.2. Optimal operation of molten slag centrifuge

The provided slag exhibited density-based separation with a false positive error rate of < 1 in 10^{32}. Molten slag separated via vertical centrifuge (L/D=1, 3000 rpm) reaches >99% separation in 84 s. If applied to all ISM slag, CO_2 emissions would be reduced by 22.8 Mtonne/year (~13% of annual Japanese ISM CO_2 emissions). The CO_2 reductions are ~3-10 times what is possible through ideal heat recovery from slag. Moreover, the CaO content can be used to offset the CO_2 generated from limestone addition (a key CO_2 source in ISM that cannot be rectified through renewable energy).

Due to the rapid separation speed, heat loss during the centrifuging process is minor and the chance for premature solidification via undercooling is low. SiO_2 and metals can reliably be expected to remain molten. The premature solidification of CaO would be likely if not for the slow separation of CaO from Al_2O_3 and SiO_2. These eutectic mixtures suppress the solidification point, making premature solidification unlikely. However, this issue requires more detailed analysis before such a centrifuge system can be reliably operated.

The potential for KHI-induced remixing of molten slags is largely negated due to the stabilizing effects of the centrifugal force. Testing and a meta-analysis of the literature revealed that the geometry of the container (L/D) acts to suppress the maximal velocity of reconfiguring liquid layers and lessen the occurrence and severity of KHI. Taking these factors into account, the stable layer velocities required during centrifuge deceleration are shown in Figure 2.

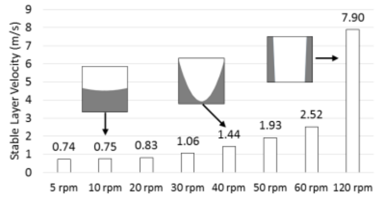

Figure 2: Stable Deceleration Regime