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This research primarily examined the use of waste oxide briquettes (WOB), prepared from blast furnace and basic oxygen furnace (BOF) dusts and mill scale, in BOFs and in particular, the reasons for and methods to reduce slopping in BOF when WOBs are used. Also, the recycling of EAF and stainless steelmaking dusts were examined. It was found that at a critical FeO content in the slag, metal drops emulsify increasing the reaction area and rate drastically, promoting slopping. Recommendations were made to delay the build-up of FeO in the slag to this critical value, thus reducing slopping. Although recycling of EAF dusts in the EAF increases energy use and decreases productivity, it provides Fe units, reduces dust disposal by 25-40%, and increases the Zn content of the dust to acceptable levels for use by Zn-producers. Stainless steelmaking dusts can also be recycled as WOBs adding Cr to the melt and generating CO gas resulting in good slag foaming.

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Although recycling of EAF dusts in the EAF increases energy use and decreases productivity, it provides Fe units, reduces dust disposal by 25-40%, and increases the Zn content of the dust to acceptable levels for the use by Zn-producers.

Stainless steelmaking dusts can also be recycled as WOBs adding Cr to the melt and generating CO gas resulting in good slag foaming.

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Abstract:

The U.S. steel industry produces over 3 million tons of waste oxides, as dusts and mill scale, per year. This research primarily examined the use of these materials in basic oxygen furnace (BOF) as waste oxide briquettes (WOBs), and in particular, the reasons for and methods to reduce slopping in BOFs when WOBs are used. Also, the recycling of EAF and stainless steelmaking dusts were examined. Slopping occurs, when WOBs are used in the BOF, because the slag contains more FeO early in the blow causing high gas generation rates in a highly foamable slag. It is found that at a critical FeO content in the slag, metal drops emulsify increasing the reaction area and rate drastically, promoting slopping. Recommendations were made to delay the build-up of FeO in the slag to this critical value, thus reducing slopping.

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EXECUTIVE SUMMARY

The U. S. steel industry produces over 3 million tons of dusts and millscale per year. These materials can be recycled in steelmaking. This research primarily examined the use of these materials in the Basic Oxygen Furnace (BOF) and in particular, the reasons for and methods to reduce slopping. The research also examined the recycling of Electric Arc Furnace (EAF) and stainless steelmaking dusts. The major findings include:

1. When waste oxide briquettes (WOBs) are used in a BOF, slopping occurs because the slag has more FeO early in the blow causing high gas generation rates in a highly foamable slag.
2. At a critical FeO content in the slag, metal drops emulsify increasing the reaction area and rate drastically. To avoid slopping, this critical FeO content should not occur too early during the oxygen blow.
3. Recommendations were developed to reduce slopping when using WOBs.
4. It seems not feasible to separate zinc oxides from zinc ferrites in EAF dusts by size.
5. Recycling of EAF dusts in the EAF was evaluated. Whereas this process increases energy consumption and decreases productivity, it provides Fe units, reduces dust disposal by 25-40% and increases the Zn content of the dust to acceptable levels.
6. Stainless steel dusts can be recycled as WOBs adding Cr to the metal and generating CO gas resulting in good slag foaming.

1.0 INTRODUCTION

The US steel industry produces over three million tonnes of waste oxide dusts per year. The major sources are blast furnace (BF), basic oxygen furnace (BOF), and electric arc furnace (EAF) dusts and mill scale. These materials should not be considered wastes but rather as valuable by-products since they contain valuable iron (Fe) units and alloying compounds. In most countries, BF and BOF dusts are recycled in sinter plants and used in the BF. However, in the US, most sinter plants have been closed and considerable amounts of dust are simply being landfilled. Also, sinter plants have significant environmental problems. EAF dusts are classified as hazardous wastes and must be disposed of in special landfills at a high cost or treated. EAF dust treatment processes have had limited success. To be economical, the Zn and Pb must be removed and sold as a raw material for Zn product, and a suitable reduced iron product produced for recycling into the EAF. In addition, dusts generated in the production of stainless steel in the EAF and argon oxygen decarburization (AOD) vessels contain valuable alloying elements; in particular, chromium and nickel should be used effectively.

An obvious but somewhat difficult use of these by-products is to recycle them directly into the steelmaking furnaces, i.e. in the BOF or the EAF. Several steel companies produce waste oxide briquettes (WOBs) from BF and BOF dusts and mill scale. These are often used in the blast furnace. However, their use in the blast furnace is somewhat limited because they soften at lower temperatures than sinter or pellets causing an increased pressure drop in the furnace and thus reducing productivity. They also cause excessive Zn build-up in the furnace, which can cause scaffolding. WOBs can also be used in the BOF but reduce scrap melting, increase the Zn content of the dust, and cause excessive slopping.

At a meeting in Pittsburgh at the beginning of the research project, slopping when using WOBs, was identified as the critical issue. Plant trials were conducted in which the FeO and basicity of the slag were measured during the BOF process with and without WOB additions. Slopping occurs when there is an increase in gas evolution into a highly foamable slag. Excessive gas generation occurs when over-oxidized slag with high FeO contents reacts with carbon in iron drops producing CO. High foamable slags are those with high viscosity. These slags have a low basicity and temperature and are present in the first 50% of the blow when slopping occurs.

EAF dusts can and are recycled into the EAF. The difficulties include increased power consumption, decreased productivity, and Zn build up in the dust. Zn build up in the dust can actually be a benefit if the Zn content can be high enough so that the dust can be used as a fertilizer or as a raw material for Zn metal production. Stainless steelmaking dusts can be recycled adding chromium to the steel but they also increase power requirements and decrease productivity.

The objectives of this work were to:

Task I. Measure the rate of reaction of FeO in slag and C in metal relevant to slopping.
Task II. Measure the foamability of slags relevant to slopping.
Task III. Make recommendations to reduce slopping when using WOBs.
Task IV. Examine the vaporization of Zn from scrap.
Task V. Evaluate the effect of recycling EAF dusts on energy consumption, productivity and Zn content of dust.
Task VI. Determine the recovery of Cr from stainless steelmaking dusts during recycle and their effect on foaming.

2.0 EXPERIMENTAL RESULTS AND DISCUSSION

The experimental techniques, results and implications of these results with respect to steelmaking operations are discussed in detail in Appendices A, B, C, D and E. The highlights are summarized below.

Task I. Extensive research was conducted on the rate of reaction of FeO in slag by C in Fe for steelmaking conditions and resulted in two publications (Appendices A and B). The experimental technique was the constant volume pressure increase (CPVI) technique, the details of which are given in Appendix A. Briefly, a piece of Fe-C alloy (2g) is heated to about 1200°C and then dropped into the slag. The moles of CO generated as a function of time are measured by the increase in pressure. The CO is from the reaction:

$$(FeO) + \underline{C} = Fe + CO \qquad (1)$$

Typical results are shown in Figure 1. As indicated in Figure 1, at about 5% FeO, the rate increases drastically and is much faster than the calculated value based on our current understanding. There must be a change in the basic mechanism.

To understand what is happening, x-ray fluoroscopy was used to view the reaction as it was happening. Below about 5% FeO in the slag, the metal droplet remained as a single drop; at higher FeO contents, the drop emulsified greatly increasing the surface area. When the reaction stopped, it reformed into a single drop. This is shown schematically in Figure 2. This is an important new finding. In fact if this did not occur, the fast decarburization reaction for the BOF would not occur.

The rate was measured as functions of temperature, FeO in the slag, Fe_2O_3 in the slag, carbon in the metal and sulfur in the metal. The results are detailed in Appendices A and B. From these, the critical condition for the fast reaction, which is necessary for slopping, were defined.

Task II. Slag Foaming: Slopping requires a high reaction rate and a foamable slag. Therefore, the foamability of slags relevant to slopping conditions was measured. The detailed experimental technique and results are given in Appendix C. The experimental technique consisted of measuring the foam volume as a function of gas flow rate through the foam. The foam index (Σ), defined by equation (2), is the accepted measure of foamability.

$$\Sigma = \frac{V_f}{Q} \qquad (2)$$

V_f = foam volume
Q = gas flow rate

In general, the foamability of a slag increases with viscosity. Therefore, a slag with low basicity, low FeO content, and at low temperatures has high foamability; these are the conditions at about 25-50% into the blow when slopping occurs. In Figure 3, the foam height in a BOF is plotted versus decarburization rate for different parts of the blow. As seen in this figure, if the fast decarburization rate occurs too early in the blow, the foam height will become excessive and slopping will occur. (See Appendix C for details).

Task III Recommendations for Reducing Slopping: Based on the results of Tasks I and II, recommendations for reducing foaming when using WOBs were developed. The details are given in Appendix B. Briefly,

1) Add the WOBs after about 30% of the blow, to reduce the chances of an over-oxidized slag when the slag basicity and temperature are higher.
2) Add the WOBs continuously to avoid excessive build up of FeO.
3) Reduce the time the lance is in the high position early in the blow to reduce the amount of FeO in the slag.
4) If all else fails, reduce the oxygen blowing rate at between 25% and 40% of the blow to decrease CO generation.

Task IV. Examination of Zn Vaporization: In general, zinc oxide (ZnO) and zinc ferrite ($ZnFeO_2$) form in EAF and BOF dust. For commercial purposes, ZnO is preferred. It's particle size in the dust is slightly larger than $ZnFeO_2$. Experiments were conducted to examine the formation of these particles. Zn was vaporized from Zn coated scrap or liquid Zn, and iron from liquid iron at a higher temperature. The condensed particles were examined using a scanning electron microscope (SEM) for their size and composition. These experiments proved to be very difficult and critical. ZnO and zinc ferrite did form in the gas phase, but there was no correlation with regards to particle size or how they vaporized. The results did not indicate whether it was possible to control the size or composition of the Zn oxides or ferrites.

Task V. Recycling EAF dusts: The effect of recycling EAF dusts on energy consumption, productivity and Zn content of the dust was evaluated using an energy and material balance for the EAF with dust as part of the charge and a dust composition model to compute the dust generated. The detailed results are given in Appendix D. Dust recycling, at a typical recycling rate of 1.1% of the charge, about 11 kg per tonne or 22 lbs. per ton of steel, increases energy consumption by about 15 kwh/tonne and decreases productivity by about 3% as shown in Figure 4. For a typical dust load of 12.5 kg per tonne of steel (25 lbs. per ton) for a normal heat, when recycling 1% dust, the dust load reaches a steady state level of 18 kg per tonne and the Zn content increases to about 50% (Figure 5). This Zn-enriched dust can be used by a Zn producer. Moreover, the amount of dust to be disposed of is reduced to 8 kg per tonne of steel.

Task VI. Recycling of Stainless Steelmaking Dusts: In the final year of the project, industry experts defined two critical issues for the recycling of stainless steelmaking dust. These are the recovery of valuable chromium and the potential of the WOBs to provide foaming. Exploratory research was conducted on the thermodynamics and kinetics of Cr recovery into the metal. The preliminary results are given in Appendix D. These results indicate that most of the Cr can be recovered. This work is continuing with funds from other sources.

Another critical issue is the use of WOBs not only to provide Cr and Ni but also to aid in foaming. When making stainless steel in the EAF, slag foaming is not as good as for carbon steels. This may be because of poor slag foamability or the inability to generate gas by the injection of carbon into the slag. The paper in Appendix E describes measurements of the foamability of stainless steelmaking slags and the relative rates of reactions (3) and (4):

$$(FeO) + C = CO + Fe \tag{3}$$
$$(CrO) + C = CO + Cr \tag{4}$$

The results in Appendix E show that liquid stainless steelmaking slags have similar foamability as those for carbon steelmaking. However, due to the low solubility of Cr_2O_3 excessive solid phases form making the slag partially solid or “chunky”, and then, the slag cannot foam. The work also shows that the reaction (3) is much faster than the reaction (4). This means that gas generation, when producing carbon steels, is better because the reaction (3) produces sufficient gas, whereas for stainless steels, the reaction (4) does not produce sufficient gas for foaming.

WOBs for stainless steel contain Cr_2O_3, FeO, CaO and C plus other minor compounds. When these are added to the slag, the C and FeO react according to the reaction (3) and good foaming results. This was demonstrated in the work discussed in Appendix C.

3.0 CONCLUSIONS

This work examined several critical issues when using recycled waste oxides in steelmaking. The major results were:

1. When using WOBs in a BOF, slopping occurs, because the slag has more FeO early in the blow, causing high gas generation rates in a highly foamable slag.
2. There is a critical FeO content in the slag when metal drops emulsify increasing the reaction area and rate drastically. To avoid slopping, this should not occur too early during the blow.
3. Recommendations were developed to reduce slopping when using WOBs.
4. It does not appear feasible to separate zinc oxide from zinc ferrite in EAF dusts by size.
5. Recycling of EAF dusts in the EAF was evaluated. Whereas this process increases energy consumption and decreases productivity, it provided Fe units, reduces dust disposal by 25-40% and increases the Zn content of the dust to acceptable levels.

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