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Abstract

Ferrous industry slag is waste product of all steelmaking manufactures. These materials should be reused or stocked. There is abundant literature on the subject of reuse and recycling of blast furnace(BF), basic oxygen furnace(BOF), electric arc furnace(EAF). However, due to the fact that ladle furnaces(LF) have only been constructed in significant numbers since the 1980's, the relatively low slag volume in comparison to the other slags and also the high variability in slag chemistry, very few papers have been published on the recycling of ladle slag as separate materials.

Studies reveal that there is significant percent calcium aluminate in ladle furnace slags which is the main compound of ladle fluxes. These fluxes are widely used to clean steel production processes. Hence, using of ladle furnace slags as a part of ladle fluxes can be considered as an economical recovery for these materials.

In current study, the LF slags of Mobarakeh Steel Company (MSC) was separated from metallic part and also was crashed and sized. This powder was blended with some minerals in order to meet different chemical composition of synthetic fluxes. Plant trials were conducted to illustrate the useful chemical composition of flux through assessing the effect of LF slag addition on some criteria such as ladle slag fluidity and raw materials consumption. Eventually, suitable compound were specified. This flux not only provided the necessary fluidity but also reduced the raw materials consumption such as lime and metallic Aluminum. From the result analyses it can be predicted that the continuous use of this synthetic flux in addition to improve desulfurization in ladle, decrease the refractory consumption.

Keywords

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RECYCLING OF LADLE FURNACE SLAGS

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Abstract

Ferrous industry slag is waste product of all steelmaking manufactures. These materials should be reused or stocked. There is abundant literature on the subject of reuse and recycling of blast furnace(BF), basic oxygen furnace(BOF), electric arc furnace(EAF). However, due to the fact that ladle furnaces(LF) have only been constructed in significant numbers since the 1980's, the relatively low slag volume in comparison to the other slags and also the high variability in slag chemistry, very few papers have been published on the recycling of ladle slag as separate materials.

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Introduction

The production of quality steel at competitive cost and in an environment friendly manner is the biggest challenge facing the steel industry today[1]. The major problems in clean steel manufacture are incomplete separation of clustered solid inclusions ($>5\ \mu\text{m}$ in diameter), the presence of sporadic large liquid inclusions due to emulsification of covering slags and the presence of solid materials that originate from the refractories used to contain steels. There is one major technique that is used to completely remove inclusions, and that is dissolution into a liquid slag. For liquid inclusions this step is not a problem, because they tend to have limited solubility in the covering slags, and the production of clean steel in which the inclusions are solid is dependent on slag chemistry, mixing in the slag, slag temperature gradient, and volume[2].

The ladle metallurgy furnace is an additional steel refining step lowers the level of elements such as sulfur and phosphorous and decrease the content of non-metallic inclusions such as alumina and various sulfide and oxide species. In the ladle refining of steel, a surface slag covering is required to provide specific chemical and physical functions. The slag composition is designed for different grades of steel being produced with the majority requiring desulphurization. Regardless of the chemical refining requirements of slag, it is advantageous for the ladle slag to become as fluid as possible immediately upon trapping the metal from the furnace into the ladle[3]. In order to meet these requirements, some prefused materials have been used in ladle furnace. A suitable ladle flux must provide the following properties[1]:

- Being basic, particularly rich in lime, in order to provide both a deoxidizing and desulphurising effect
- Being liquid at the steel temperature in order to cover the metal properly
- Having a high desulphurising capacity (typically the case of lime-saturated slags)
- Reduction of O,N and H pick up into the metal
- Avoid of fluorspar usage, which is harmful to the environment and to the refractories
- Permission of more intense stirring of the metal and slag with less risk of reoxidation, thus making it possible to speed up the desulphurising of the metal and to reduce ladle processing time

However, calcium aluminate is very expensive. Lower cost substitutes include the use of byproducts of factories such as ferrovanadium manufacture[3]. A number of solid wastes are generated at various stages of steel processing. Chemical composition of waste materials determines whether they can be recycled[1]. There are abundant literature on the subject of steelmaking byproducts recovery. But very few papers have been published on ladle slag as a separate material. This is likely due to[4]:

- The fact that ladle furnaces have only been constructed in significant numbers since the 1980s
- The relatively low slag volume compared to the other slags
- The high variability in slag chemistry due to the large variety of secondary steelmaking processes

Since the LF slag has high CaO content, it was thought that the slag would be a good material for recycling at the LF, particularly with respect to replacing part of lime addition made

during LF treatment. In addition, it is also a prefused materials which is able to provide some fluidizing action, as well[1].

Kumar et al[1] tried to recycle LF slag in Tata steel. They developed a synthetic slag briquette consisting of high calcium lime, recycled stove brick and recycled ladle furnace slag. They found that since recycled LF slag has low levels of acidic oxide, sulfur and phosphorous, a large volume of this material can be used to provide a suitable slag covering with high refining capability.

A typical analysis of LF slag which had been used by this group of researchers is shown in table 1. The synthetic slag employed was a coarse blend of 40% recycled LF slag, 40% high calcium lime and 20% dolomite lime. The raw LF slag had transported to a plant where the raw LF slag was separated. The non-magnetic fraction of 8-80 mm size, was further screened to 10-40 mm size. Results had shown that the addition of ~200 kg/heat of LF slag does not alter the ladle slag composition significantly. Although the basicity of slag decreased, the desulphurization behavior of slag did not changed. Moreover, during six months LF slag recycling in Tata steel, average consumption of fluorspar and lime decreased 30% and 5% respectively[5].

Table 1. Typical analysis of LF slag in Tata steel

Component	CaO	Al ₂ O ₃	SiO ₂	MgO	MnO	S	P ₂ O ₅	Fe(T)
Percent	50-55	25-35	3-6	8-10	~0.1	~0.5	< 0.1	~1

A typical composition of LF slag at Dofasco recycled by Pinhey et al.[4] is shown in table 2. Raw LF slag sent to grinding plant, after separation of metallic part, in order to get powder under 3 mm. Based on the chemistry of slag powder, a final mix was blended using calcium and calcined bauxite to meet the chemistry and size specifications for Dofasco's LMF. Analysis of trial and regular calcium aluminate of Dofasco is shown in table 3.

Table 2. Typical composition of LF slag in Dofasco

Component	CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	MnO	P ₂ O ₅	S
Percent	50	29	6	9	2.8	1.8	0.4	0.5

After six months of operation, results indicated that the sulfur removal improved significantly from 26.5% to 34%. The use of 20% ladle slag calcium aluminate at Dofasco's LMF resulted a 15% cost saving in the purchasing of synthetic flux and also reduced the amount of ladle slag for disposal.

BPI company is one of synthetic ladle flux producers. Table 4 illustrates the various fluxes produce in this factory for steelmaking companies. It is obvious that a wide range of flux composition can be used in ladle furnaces. Thus, different compositions tested in Mobarakeh Steel Company to meet a suitable one.

Table 3. Analysis of trial and regular calcium aluminate at Dofasco

Component	Calcium Aluminate (wt%)	
	Regular	Trial
Al ₂ O ₃	62-67	62.9
CaO	20-25	20.3
MgO	10-15	9
SiO ₂	1	2.5
V ₂ O ₅	2	1.2
FeO + MnO	1.3	1.9
S	<0.06	.05
Na ₂ O	-	0.3
P	<0.02	0.01

Table 4. BPI ladle synthetic fluxes

Component Product	CaO	Al ₂ O ₃	MgO	SiO ₂	Fe ₂ O ₃	S	P ₂ O ₅
Syn-Slag79	76-82	3-7	0.5-2.5	0.5-2.5	<0.3	<0.05	<0.05
Cal Flux 47R	29-35	44-50	6.5-9.5	4.5-8.5	<2.5	<0.3	<0.1
Cal Flux 50-W2	19-25	47-53	11-17	6-10	<2	0.1-0.3	-
Cal Flux 62K	30.7-34.7	58.5-64.5	0.2-2.2	1.2-3.2	1.1	0.2	0.1
Cal Flux 72-N	9-15	69-75	7-13	<2	<0.6	0.05	0.06
Cal Flux 44K	43.8-47.8	40.8-46.8	0.3-2.3	2.2-4.2	1.4	0.2	0.1

Experimental

Mobarakeh Steel Company(MSC) has four 200 ton ladle furnaces. The amount of slag generated per heat is about 2 ton. The slag of six ladle of Al-killed steels collected and separated the metallic part by magnetic system and remained slag crushed and screened to reach powder under 2.5 mm. The chemical composition of powder is shown in table 5. Then final powder blended in with calcined bauxite and high calcium lime to get compositions shown in table 6. Industrial trials drew up as below.

Table 5. Typical composition of LF slag at Mobarakeh Steel Company

Component	CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	MnO
Percent	49	28	6.4	8.6	4.9	1.9

At the first experiment, 300 kg of sample 1 of table 6 as well as 700 kg lime added to the ladle during tapping of EAF. It should be mentioned that 700 kg lime addition to the ladle is currently standard practice at Mobarakeh Steel Company. The other process designed by adding 300 kg of sample 2 of table 6 together with 400 kg lime. At the third trial, 400 kg of

sample 3 mixed with 400 kg lime and added to ladle during tapping. It should be noted that slag fluidity evaluated through observation. Finally, lime and Aluminum consumption determined in every process and compared with average consumption of factory.

Table 6. Chemical composition of various trial synthetic fluxes

Component Sample	CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	MnO
1	33.4	46.2	5.4	7.5	1.6	0.6
2	49	28	6.4	8.6	4.9	1.9
3	37	40	6.4	8.8	3.7	1.4

Results and discussion

The first component caused a rarely fluid slag but its amount was too high. With respect to the chemical composition of entry and exit slag of ladle furnace shown in table 7, it can be recognized that its suitable fluidity was due to high percentage of FeO in entry slag. High percentage of FeO and MnO in slag lead us to change the composition of synthetic flux. So at the second trial 300 kg of sample 2 together with 400 kg lime were added to ladle. Slag thickness and also FeO and MnO percent (table 8) were lower than previous experiment significantly. High percent of Al₂O₃ in slag might cause high percent of calcium aluminate in slag which is able to improve slag fluidity. For this reason, 400 kg of sample 3 and 400 kg of lime were added to ladle. Chemical composition of exit slag of these trials are summarized in table 9. Low percentage of FeO and MnO and adequate fluidity lead us to choose it as the best composition. Presence of 10% MgO in above component would reduce ladle slag zone wear in a lengthy usage.

Table 7. Chemical composition of entry and exit slag of LF with sample 1

Component LF slag	CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	MnO
Entry	46.05	10.2	7.67	7.25	14.73	12.69
Exit	54.15	18.95	5.2	6.5	6.5	7.35

Table 8. Chemical composition of entry and exit slag of LF with sample 2

Component LF slag	CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	MnO
Entry	46.3	17.5	5.8	11.2	9.9	6
Exit	45.4	26.3	4.5	12	5.96	3.5

Table 9. Chemical composition of entry and exit slag of LF with sample 3

Component Melt No	CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	MnO
160282	55	25.5	4.7	10	2	0.5
180297	38.5	38.5	7	11.5	0.4	-

However, average consumption of lime and Aluminum determined in different trials and compared with average consumption of the other melts. The mean consumption of lime for trials in ladle furnace was 300 kg while this amount was 520-530 kg for the other ladles. There was a fact that 400 kg lime addition during EAF tapping caused to reduce lime consumption around 500 kg/heat. Moreover, average aluminum usage per heat was 1.5 kg/ton while it was 1.6 kg/ton for normal melts of factory.

Conclusion

Industrial trial results showed that:

- Ladle slag could be used up to 75% in synthetic flux without adversely affecting the operation or steel chemistry
- Reduction of 600 kg lime consumption per heat
- Reduction of 0.1 kg/ton Aluminum consumption
- Improvement of slag chemistry in ladle furnace

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