



DOI: 10.31643/2021/6445.44

Modification of microstructure of LD slag for recovery of hybrid flux material

^{1,3}Dilip M., ^{1,2}Rajendra K.R.

¹Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, India

²CSIR-National Metallurgical Laboratory (NML), Jamshedpur, India

³Research and Development Division, Tata Steel Ltd, Jamshedpur, 831001, India

* Corresponding author email: dmakhija14@gmail.com

ABSTRACT

The Basic Oxygen Furnace steel making process produces BOF slag (LD slag) at a rate of about 125 kg/t. The LD slag contains about 18% Fe in wustite and dicalcium ferrite and about 45% CaO. These minerals are an excellent source of alternative flux material for the steel industry. Through slag modification and in-depth characterization studies, investigations were carried out to develop a material that could be utilized as an alternative flux material. Detailed characterization studies were conducted using SEM-EPMA and XRD to identify the changes in the crystal structure, phase distribution, grain size and liberation size of minerals. The grain size of phases was found to be between 10-150 μm for normally cooled slag and 20-250 μm for slowly cooled slag. It was also shown that slow cooling promotes the formation of an additional phase which is essentially the dicalcium silicate phase (C_2S) with some amounts of FeO and MgO in the crystal lattice. Overall, it was observed that about 50% of the LD slag could be recovered as alternative flux material containing approximately 30% CaO and 30% Fe content. This alternative flux material is an excellent source of material for use in steel industries because of its low melting slag formation.

Keywords: LD slag, characterization, hybrid flux, cooling rate, microstructure.

Information about authors:

Dilip Makhija

Doctoral candidate, Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India; Research and Development Division, Tata Steel Ltd, Jamshedpur, 831001, India. E-mail: dmakhija14@gmail.com, <https://orcid.org/0000-0002-5011-2671>

Rajendra Kumar Rath

Senior Principal Scientist, Mineral Processing Department, CSIR-National Metallurgical laboratory, Jamshedpur, 831007, India; Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, India. E-mail: rkrath@nmlindia.org

Introduction

The ferrous metallurgical slag mostly consists of granulated BF slag and Steel slag cooled in the air, known as Linz Donawitz (LD) or Basic Oxygen Furnace (BOF) Slag. The distribution of BF slag and Steel slag is about 58% and 42% respectively. The specific rate of generation of LD slag from steel making process is about 125 kg/ton [1-4].

The LD slag tapped out of the converter may sometimes contain up to 25% metallic iron, which needs to be recovered to minimize metal losses [5]. The non-magnetic LD slag has useful mineral phases like dicalcium silicate (C_2S), tricalcium silicate (C_3S), dicalcium alumino ferrite, magnesio-wustite and some amount of free lime [5]. It has also been reported that LD slag may contain some amount of periclase, Mn cordierite and glass content [6].

The non-metallic LD slag has a basicity of greater than 3 in view of higher CaO content which goes as high as 50% in some cases. The CaO is present in the form of dicalcium and tricalcium silicate and free lime. Since free lime tends to stabilize in the presence of water, it gets converted to portlandite $\text{Ca}(\text{OH})_2$ which ultimately results in volumetric instability and expansion of the slag or any structure made out of the non-metallic slag [7]. The expansion is associated with the cracking of the structures over some time. The expansion is also caused due to the presence of free MgO (periclase) which is the cause of delayed expansion and cracking [8-9].

Many literatures report that using LD slag as a flux material improves the iron ore sintering efficiency, and this is because of the fast melt formation during the sintering process. In addition, the iron oxide present in non-metallic LD slag also

adds to the iron burden, thereby reducing the specific consumption of iron ore [10-11]. The constraint, however, is because of the high phosphorus content of LD slag which restricts its usage in iron ore sintering [12].

Extensive research has been done over the last 40 years on stabilizing LD slag to make it suitable for civil engineering applications. Research has also been done in recycling and reuses applications within the steel industry [13-16].

It is reported that the use of non-metallic LD slag in Bhilai Steel Plant, India, was discontinued due to the higher content of Phosphor and Sulphur [17]. The phosphorus removal from LD slag is a much-researched topic and, several studies have been carried out on this subject [18-23].

The bulk utilization of LD slag through CO₂ sequestration has also been attempted and it is reported that about 6-11% of the CO₂ generated from LD converter can be sequestered using LD slag [24].

The research work available so far suggests that not much research has been done on the recovery of hybrid flux material, which contains both lime and iron oxide. Therefore, this research work focuses on the objective to develop enablers for synthesizing a material that is a hybrid material containing lime and iron oxide and has excellent slag met properties when used in the iron making process.

The research work presented in this paper is attempts to develop enablers through preliminary modification and characterization studies of modified slag.

The modification of crystal structure promotes grain growth and segregation of elements in various, thereby providing an opportunity to separate iron and calcium ferrite-based phases as hybrid materials. The detailed characterization studies were carried out to reveal the grain size, crystal structure, elemental distribution in various phases and the degree of liberation. The studies were conducted for two different cooling. The standard industrial practice of cooling in 3 hours and an extended period of 6 hours were chosen for revealing the changes in the above characteristics.

Materials and Methods

LD Slag. The LD slag used for various experiments was obtained from Tata Steel Ltd (Jamshedpur, India). As explained in the preceding section, the slag treatment process at Tata Steel Ltd, Jamshedpur, consists of crushing the material up to

6mm, followed by metal recovery. The non-metallic slag generated after the recovery of metallic iron was taken for conducting the experiments since this is a significant area of concern. The non-metallic slag size 0-6mm comprises substantial chunk of the total slag volume generated during steel making in LD converters.

Characterization. The chemistry of LD slag non-metallic rejects taken for research studies was performed Using-Inductively coupled plasma spectroscopy (ICP-MS). Figure 1 presented below shows the total composition of LD slag

The as-received LD slag was subjected to particle size distribution to understand the distribution of various oxide phases in different size classes. Table 1 presents the data obtained on particle size distribution that was carried out using sieve analysis.

The particle size distribution data suggests that the distribution of iron oxide is relatively more in coarser fractions than the finer fractions. This indicates that the relative size of wustite grains is more than the C₂S and C₃S grains. The weight retained on various sieves from coarse to fine size is presented in Table 1. The d₅₀ particle size of the slag is about 1.1mm.

The particle size distribution also suggests that hydrated phases are more in the more acceptable size classes, which is evident from the higher loss on ignition content (LOI). The coarser size classes show relatively lower LOI% while the same is as high as 16% for the finest size class of -0.075mm. Therefore, it can be concluded from this that the free lime and MgO content disintegrate during crushing and reports to the acceptable size class where it hydrated in the presence of water when the slag is cooled.

As discussed earlier, a grade wise distribution of Fe suggests that the particles that the coarser particles are rich in iron content while the finer particles are lower in iron content. The grindability of the iron-rich wustite and ferrite is a possible reason behind the preferential segregation of iron grains. The rationale put here for the difference in the grade of coarse and fine particles also agrees with few research works conducted on studying the of grindability of steel slag. The work done by Wang et al. [25] also found similar results when studying the cementitious property of steel slag powder based on their size. In this study, XRD studies were conducted with fine and coarse fractions of steel slag, and it was observed that coarse particles contained more of RO phase and wustite phase while the finer fractions contained more C₃S and C₂S.

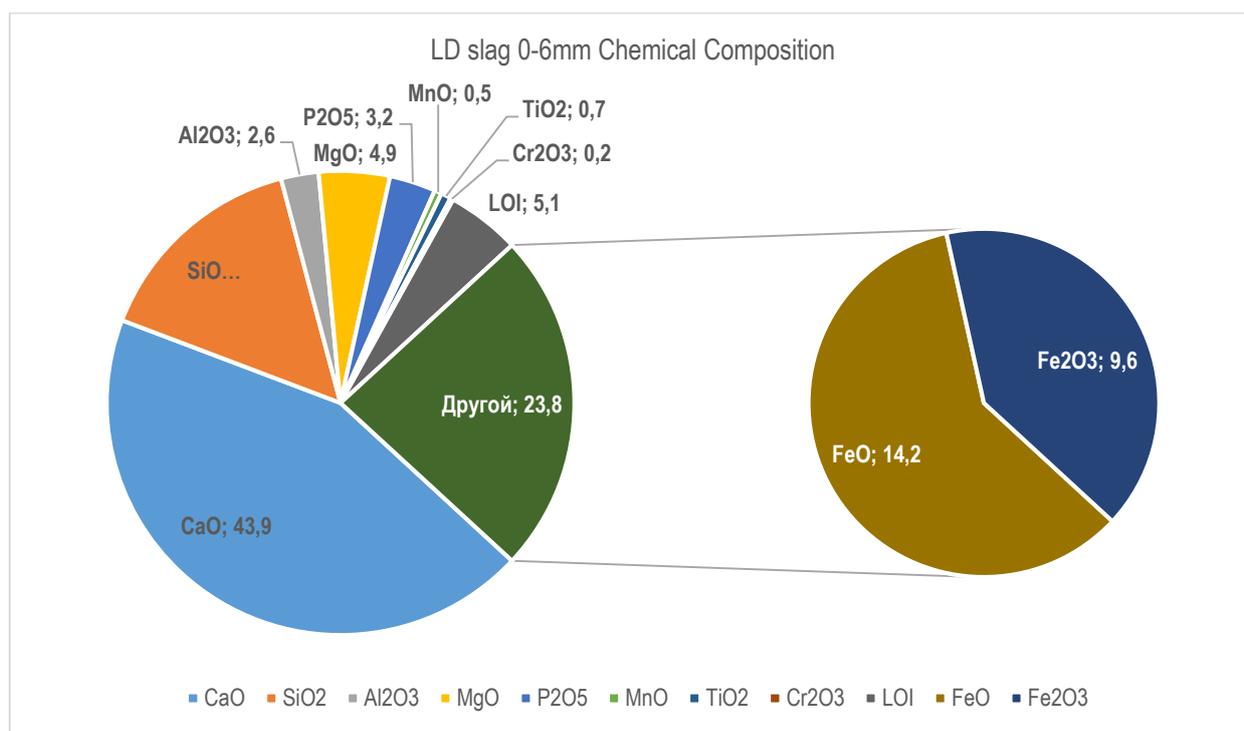


Figure 1 - Chemistry of as-received LD slag

Table 1 - Sieve analysis of as-received LD slag

Size(mm)	Wt%	Fe(T)%	FeO%	SiO ₂ %	CaO%	Al ₂ O ₃ %	MgO%	P%	LOI%
-10+6	13.8	17.88	18.06	14.96	45.45	2.54	4.75	1.34	4.5
-6+3	18.6	20.92	20.64	14.03	44.57	3.38	4.54	1.34	3.8
-3+1	22.2	21.01	20.64	15.3	43.62	2.79	4.06	1.36	4.1
-1+0.5	4.9	20.53	26.49	15.95	40.84	2.73	5.12	1.36	4.3
-0.5+0.25	25.1	16.67	12.77	15.4	43.9	2.48	5.55	1.42	8.9
-0.25+0.15	4.1	14.52	12.9	15.04	43.25	2.11	6.39	1.48	11.1
-015+0.1	3.3	15.43	11.87	14.15	44.15	2.28	5.22	1.6	13.6
-0.1+0.075	3.3	15.44	10.32	13.67	43.2	2.66	5.2	1.62	14.6
-0.075	4.7	11.94	7.22	13.87	43.56	3.38	6.01	1.65	17.4
Total	100	18.38	17.01	14.90	43.96	2.76	4.93	1.40	6.88

Modification of LD slag through controlled cooling rate. The LD slag was modified in two ways:

1. Re-melting and cooling in the crucible for 3 hours followed by cooling in the atmosphere
2. Re-melting and cooling in the crucible for 6 hours followed by cooling in the atmosphere.

The re-melting of the solid slag was carried out in a graphite crucible in a furnace capable of

achieving a temperature of 1800°C. The solid slag sample was melted by heating at a rate of 6-8 °C/minute. The slag sample was melted entirely over 5 hours.

After melting the slag sample, the same was allowed to cool as per the cooling pattern mentioned above. The graph depicting the cooling rate of the melted slag samples is shown in Figure 2.

The slag cooled over 3 hours was named as typically cooled slag and the slag cooled over 6 hours was called as slowly cooled slag.

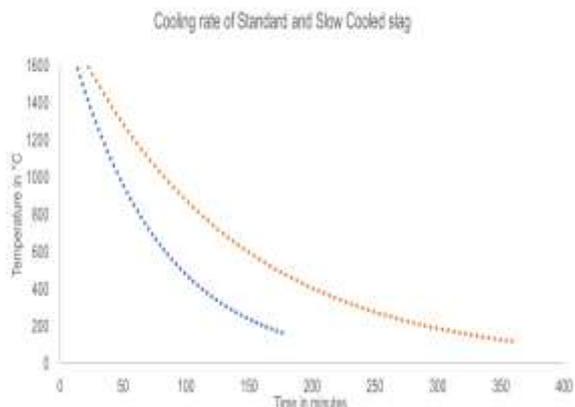


Figure 2 - Cooling rate of LD slag for 3 hours and 6 hours of the cooling period

Results and Discussion

Elemental Mapping of Normal Cooled Slag. The LD slag was characterized using SEM-EDS and the preliminary images and the mapping of various elements as shown in Figure 3. Table 2 presented below gives the pointwise mapping of various elements. The SEM image distinguishes various phases in terms of different shades of black, white and grey colour.

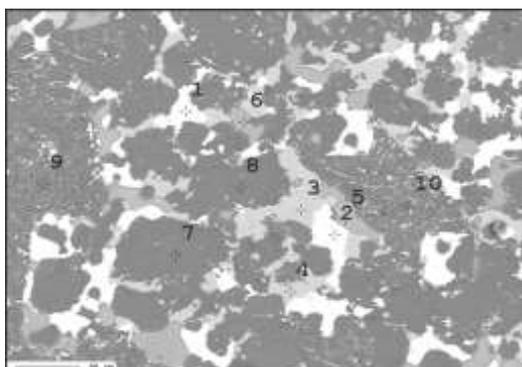


Figure 3 - SEM image of as-received LD slag showing different phases marked with numbers

Odd metal droplets are also seen in the SEM image, which is very fine in size, which suggests that these metal droplets are entrapped in the slag matrix. The EDS elemental mapping shows darker black phases, which are calcium silicate phases having lower atomic mass. The metal oxide phases containing FeOx, MgOx and MnOx are identified as lighter phases. The magnification of the microscope

clearly distinguishes various phases and it can be seen that the size of the crystal of various phases is of the order of only a few μm .

Figure 4 presented below shows the XRD image of the as-received LD slag. The XRD analysis to identify the phases confirmed the findings of SEM analysis. The primary phases present include dicalcium silicate, tricalcium silicate, wustite, calcium ferrite and magnesio ferrite phase. The presence of these phases was also confirmed from the XRD analysis.

The SEM elemental mapping image and the composition suggest that the light phase combines calcium ferrite and the RO phase. The SEM elemental mapping shows the composition of various phases, and it is observed from the data that the dicalcium silicate phase also contains about 4-6% P_2O_5 . Similarly, the tricalcium silicate phase also includes P_2O_5 but is considerably lower than the dicalcium silicate phase. The elemental mapping results suggest about 2% presence of P_2O_5 in the C_3S phase. Further, when looking at the data of light phases such as magnesio ferrite and calcium ferrite, it is observed that the proportion of phosphorus distribution is much lower in these phases and only about 0.3% P_2O_5 maximum is observed in these phases. The elemental mapping data also suggests that the calcium ferrite phase contains a considerable amount of Al_2O_3 , which goes up to 6% in most cases. The C_3S phase containing a higher amount of phosphorus more significant is unstable beyond 2% is P_2O_5 and dissociates into C_2S and CaO . Thus it is seen that C_3S includes only up to 2% P_2O_5 . This theory has also been supported in few published literature works [26].

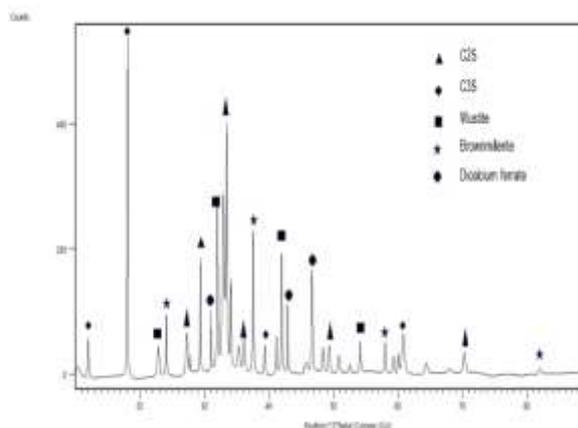


Figure 4 - X-ray diffraction image of as-received LD slag

The phase quantification was done using image scanning software, and the same was corroborated with the results of chemical analysis and XRD

Table 2 - Elemental mapping of various phases corresponding to Figure 3

Mineral	1	2	3	4	5	6	7	8	9	10
SiO ₂	24.78	0.00	0.02	0.55	1.30	0.00	0.00	28.32	27.64	21.70
Al ₂ O ₃	0.98	0.01	0.02	6.25	6.30	0.02	0.01	0.12	1.25	0.70
MgO	0.17	14.29	12.18	0.98	0.83	0.46	0.49	0.00	0.02	0.04
Na ₂ O	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.01	0.00	0.00
TiO ₂	0.82	0.00	0.07	7.90	8.69	0.00	0.01	0.32	0.37	0.29
CaO	63.51	9.24	10.48	48.93	49.18	58.82	58.89	65.81	65.66	72.02
K ₂ O	0.03	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
FeO	4.20	74.59	75.23	35.11	33.21	39.91	39.78	0.84	0.83	3.21
MnO	0.05	1.86	1.99	0.05	0.19	0.78	0.79	0.00	0.03	0.22
P ₂ O ₅	5.31	0.00	0.01	0.21	0.29	0.01	0.00	4.57	4.18	1.55
Phase	Ca-Si-O	Fe-Mg-O	Fe-Mg-O	Ca-Fe-Al-O	Ca-Fe-Al-O	Fe-Ca-O	Fe-Ca-O	Ca-Si-O	Ca-Si-O	Ca-Si-O

Table 3 - Quantification of various phases in Normal Cooled LD slag

Phase quantification from XRD corroborated from	
Dicalcium Silicate (2CaO.SiO ₂)	35.0%
Tricalcium Silicate (3CaO.SiO ₂)	17.2%
Magnesio Wustite (Fe _{0.7} Mg _{0.3} O)	20.1%
Dicalcium ferrate (Ca ₂ Fe ₂ O ₅)	14.5%
Dicalcium Alumino ferrate(Ca ₂ (Al _{1.3} Fe _{0.7})O ₅)	7.1%
Lime (CaO)	6.1%

studies. Table 3 presented below shows the quantification of various phases that are present in normally cooled LD slag.

The mineral modal analysis was carried out using SEM to understand the grain size of various phases and evaluate a separation size of phases based on their liberation size, which depends on the presence of various phases in different size classes. The images of SEM taken for the steel slag sample subjected to modal analysis is shown in Figure 5, along with the elemental mapping of the sample.

The elemental mapping shows the concentration of the element in different grains present, and it also shows the relative grain size of different phases. Figure 6 shown above was captured for estimating the liberation size of various

phases. The grains were compared on a relative scale of 200 μm, as shown in Figure 6. Based on the available results, it is seen that the grain size of iron-bearing crystals range from 25-150 μm, with most of the crystals being in the coarser range. Similarly, the image taken for mapping of calcium phase shows a crystal size of such phases in the range of 50-300 μm.

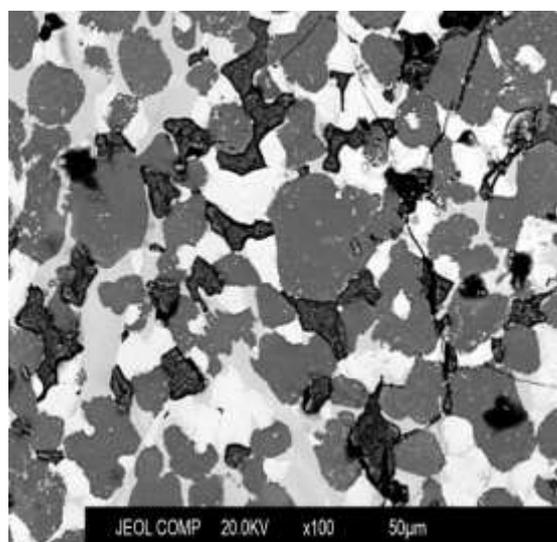


Figure 5 - SEM image of as-received LD slag for modal analysis

Comparative results on grain size, crystal structure and phases of Slow and Normal Cooled Slag. Figure 7, shown below, is the SEM image of the LD slag cooled under a slow cooling rate in the furnace.

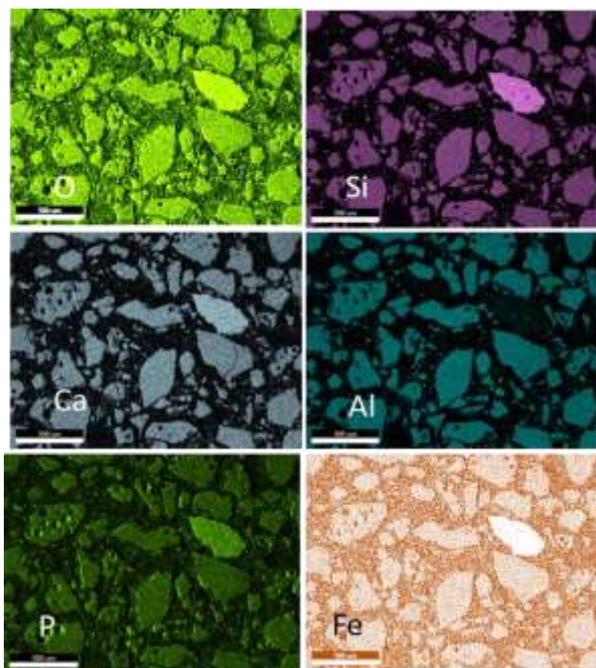


Figure 6 - Elemental mapping and liberation size analysis of as-received LD slag

It is seen from the image and Table 4 that the point 1 and 2 which was determined to contain 100% metallic Fe is much larger compared to the metallic Fe that was present in the LD slag that was cooled under standard cooling rate. It is also seen that the phases dicalcium ferrite and the calcium aluminoferrite are much larger compared to the same under standard cooling rates. Similarly, the grain size of the dicalcium silicate phase is large. The significant difference, however, was the presence of two more phases which were identified through elemental mapping. These phases are primarily the dicalcium silicate phases which have formed a solid solution with iron and magnesium. This data suggests that the slower cooling rates promote the

crystallization of new phases, and, the grain growth of the phases is also seen under slower cooling rates.

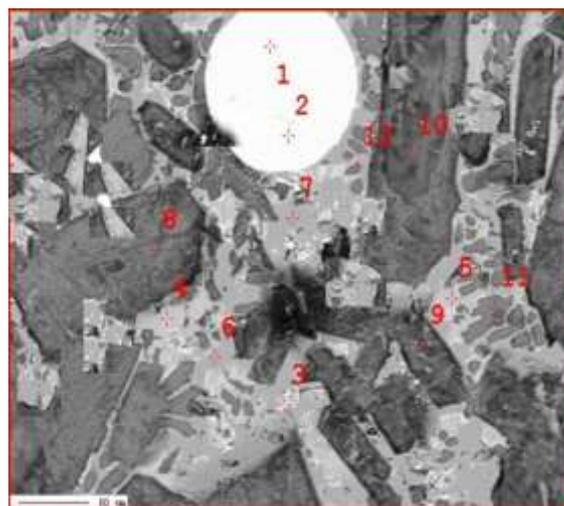


Figure 7 - SEM image of slowly cooled slag

The additional phase of Ca-Si-Fe-Mg-O contains almost the same distribution of iron as seen in the calcium ferrite phase. The composition of this new phase shows about 35% FeO. The slowly cooled slag shows a higher distribution of iron content in this phase and is about 41% compared to 35% in standard cooled slag. The formation of this new phase opens the possibility of recovering iron values simultaneously with calcium minerals as a hybrid flux material.

The SEM image of the two types of slags was taken for capturing the data on liberation size and the grain size of individual phases. The images as shown below in Figures 8 and 9 indicate that the grain size of separate phases under a slow cooling rate is relatively more than that under standard cooling conditions.

Table 4 - Elemental mapping corresponding to Figure 7

Mineral	1	2	3	5	6	7	8	9	11	12
SiO ₂	0.03	0.06	18.19	8.56	1.77	2.00	21.01	24.35	21.36	19.16
Al ₂ O ₃	0.00	0.03	0.91	0.02	4.50	4.24	0.7	1.95	1.06	0.51
MgO	0.01	0.00	3.96	0.32	0.48	0.44	0.08	0.15	0.15	3.07
Na ₂ O	0.02	0.00	0	0.03	0.00	0.00	0.00	0.00	0.00	0
TiO ₂	0.01	0.03	0.39	0.09	9.47	8.37	0.35	0.45	1.94	0.42
CaO	0.00	0.00	40.08	21.46	41.49	43.11	71.21	65.97	64.38	43.65
K ₂ O	0.00	0.00	0.03	0.00	0.01	0.00	0.01	0.04	0.06	0.02
FeO	99.89	99.88	34.50	68.24	41.57	41.35	2.43	2.07	3.07	32.12
MnO	0.02	0.00	0.31	1.26	0.08	0.10	0.26	0.05	0.03	0.16
P ₂ O ₅	0.01	0.00	0.76	0.04	0.63	0.49	1.98	4.97	7.92	0.88
Name	Fe	Fe	Ca-Si-Mg-Fe-O	Ca-Fe-Si-O	Ca-Fe-Al-O	Ca-Fe-Al-O	Ca-Si-O	Ca-Si-O	Ca-Si-O	Fe-Mg-Ca-Si-O

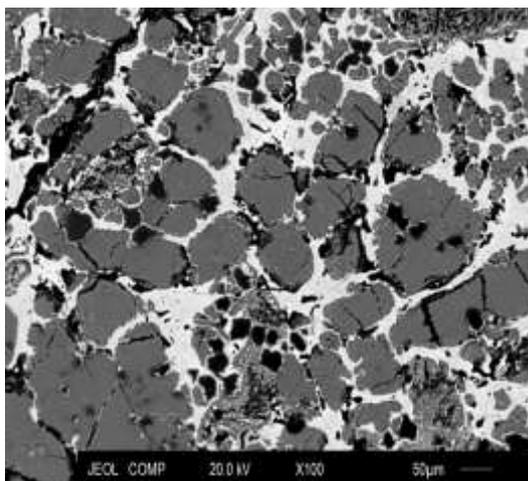


Figure 8 - SEM image of slowly cooled slag

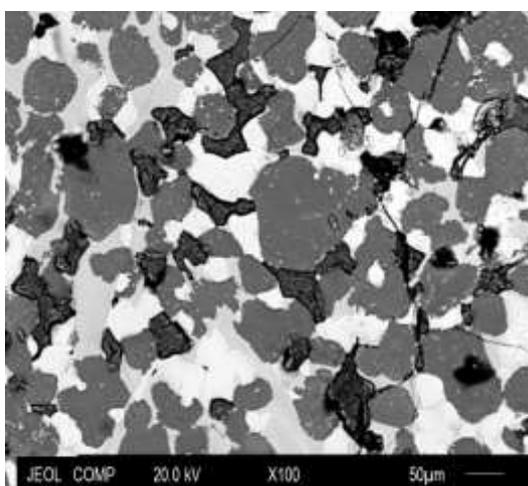


Figure 9 - SEM image of normally cooled slag

The Table 5 shows the data pertaining to the grain sizes of various phases for slags cooled under normal and slow cooling rates.

Table 5 - Grain size of crystals in slow and normal cooled slag

Phase	Standard cooling rate (3 hours)	Slow cooling rate (6 hours)
	Grain Size (µm)	
Dark-coloured C ₂ S and C ₃ S phase	10-150	50-150
Light-coloured Iron bearing phase	10-100	20-150

Table 5 shows the data obtained with SEM-EDS and corroborated with XRD studies. The results suggest that the slowly cooled slag contains an additional phase of dicalcium silicate with a high amount of Fe and Mg content, and the total content of this phase is about 6.2%.

The XRD image presented in Figure 10 below suggests that a new phase containing dicalcium silicate primarily with iron and magnesium oxide emerges when the slag is cooled slowly. It is also seen that the C₃S phase in slowly cooled slag is comparatively lower than standard cooled slag.

Further, the peak intensity in the case of slowly cooled slag also indicates the changes in concentration of individual phases. Higher peak intensity for many phases in slowly cooled slag implies that the mineral phases become richer in grade with the significant mineral. Further, the XRD results of a new phase are also corroborated by the SEM elemental mapping, which shows a new phase containing Fe-Mg-Ca-Si-O elements.

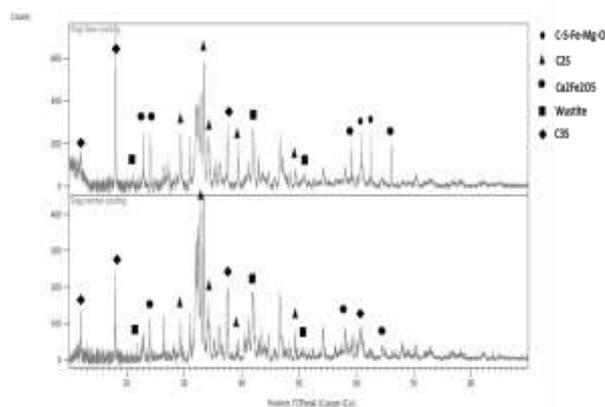


Figure 10 - XRD image of slowly cooled slag showing a new phase

The phase-wise distribution of various phases as calculated from SEM and XRD data is presented in Table 6 below.

It is seen from the results that the individual phases like dicalcium ferrite, tricalcium ferrite and calcium ferrite have all reduced by a smaller proportion and a new phase composed of Fe-Mg-Ca-Si-O has emerged, which is about 6.1% in total.

Therefore, as confirmed by the characterization studies, the basis for separating iron-rich minerals from the slag should be to slowly cool the slag slowly, thereby allowing maximum time for crystallization and growth of phases. The cooling rate is an essential parameter in grain size control [27-28]. A slower cooling rate helps migrate more calcium minerals to the iron-bearing phase of

calcium ferrite and more iron in the calcium bearing phase Ca-Si-Fe-Mg-O.

Tables 7 and 8 presented below show various phases' distribution in LD slag cooled under standard and slow cooling rates.

The mineral liberation analysis of normal and slow cooled slag is shown in Figures 11 and 12.

The graph indicates that the liberation of the C_2S and C_3S phase from iron-bearing phase is much better in the case of slowly cooled slag especially at the coarser size (0.25-0.5mm). The degree of liberation at this size for standard cooled slag is about 50%, while the same value for slowly cooled slag is about 75%. The liberation of these phases at other size classes is marginally better for slowly cooled slag. The degree of liberation is defined as the number of particles in a size class that is at least 80% liberated from each other.

By the above explanation, it can be inferred that in size range of >0.05 mm, the grains with at least 80% degree of liberation are presently more than 90% in standard cooled slag. Similarly, for the case of 0.25-0.50mm size range in standard cooled slag, the

grains with a degree of liberation greater than 80% are present only 50%. This means that the grain size in this size range has 50% non-liberated grains, which have a degree of liberation of less than 80%.

Figures 13 and 14 below show the cumulative weighted average liberation of 0-0.5mm LD slag for normal cooled and slow cooling conditions.

The significant difference between the two cases can be seen in the weighted average liberation of 0.5-0.25mm size class. The standard cooled slag shows only about 18% liberation, while the slowly cooled slag indicates approximately 27% liberation. The cumulative liberation of slowly cooled slag, 80.9%, is mostly the result of higher liberation in 0.5-0.25mm fraction, and almost 80% of this difference is coming from this size class. The size class 0.25-0.10mm contributes about 1% to the difference in cumulative liberation. The data indicates that the slowly cooled slag can be efficiently separated at the same grind size compared to standard cooled slag. The difference in liberation by 10% will improve the yield and the grade of concentrate.

Table 6 - Phase quantification of Slow Cooled and Standard Cooled slag

Phase quantification from XRD corroborated from Chemical analysis	Wt%	
	Normal Cooled	Slow Cooled
Dicalcium Silicate ($2CaO.SiO_2$) with Phosphate phase	35.0	32.7
Tricalcium Silicate ($3CaO.SiO_2$) with Phosphate phase	17.2	16.5
Magnesio Wustite ($Fe_{0.7}Mg_{0.3}O$)	20.1	18.5
Dicalcium ferrate ($Ca_2Fe_2O_5$)	14.5	13.4
Dicalcium Alumino ferrate($Ca_2(Al_{1.3}Fe_{0.7})O_5$)	7.1	6.6
Lime (CaO)	6.1	6.1
Dicalcium silicate with Fe-Mg	Nil	6.2

Table 7 - Distribution of various phases as a function of size class in normally cooled slag

Size fraction(mm)	Wt%			
	C_2S & C_3S	Mg-Fe-O	Ca-Fe-O	Ca-Fe-Al-O
0.25-0.5	58	24	10	8
0.10-0.25	62	21	11	6
0.05-0.10	65	15	14	6
-0.05	67	14	12	7

Table 8 - Distribution of various phases as a function of size class in slowly cooled slag

Size fraction (mm)	Wt%				
	C ₂ S & C ₃ S	Mg-Fe-O	Ca-Fe-O	Ca-Fe-Al-O	Ca-Si-Fe-Mg-O
0.25-0.5	58	20	10	6	6
0.10-0.25	59	19	11	5	6
0.05-0.10	61	18	11	4	6
-0.05	62	17	12	4	5

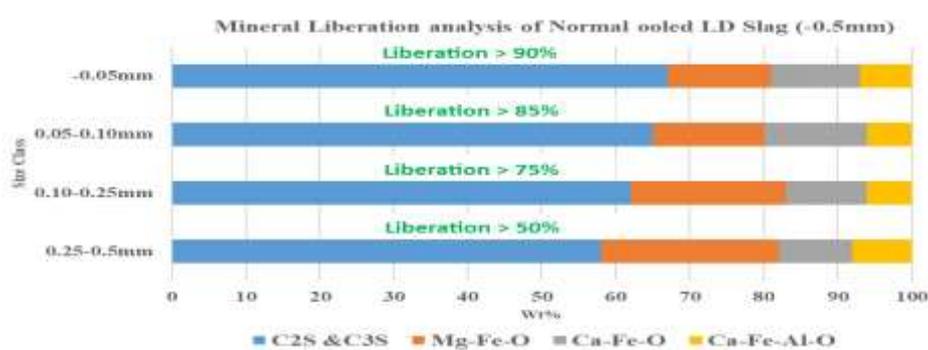


Figure 11 - Mineral liberation analysis of normally cooled slag at 0.5mm grind size

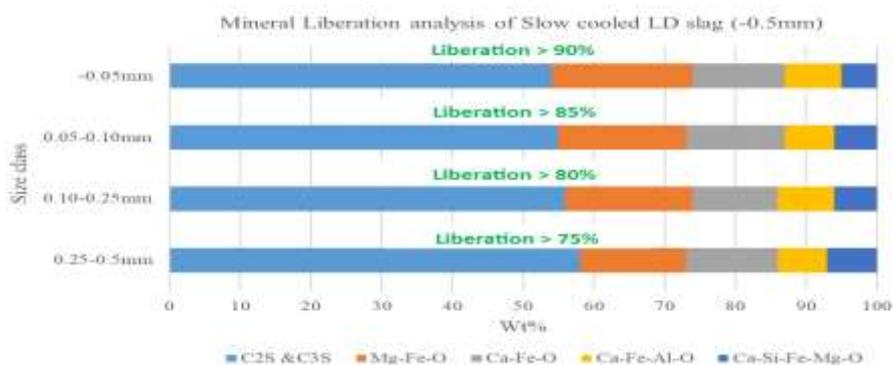


Figure 12 - Degree of liberation of slowly cooled slag at 0.5mm

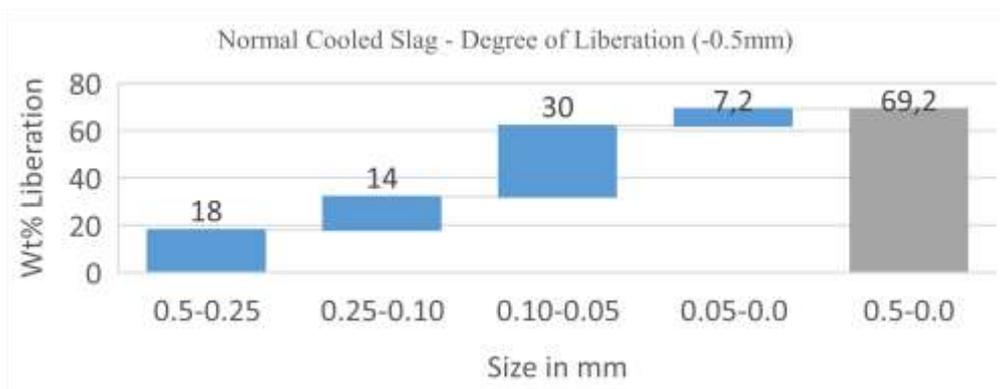


Figure 13 - Cumulative degree of liberation of normally cooled slag at 0.5mm size

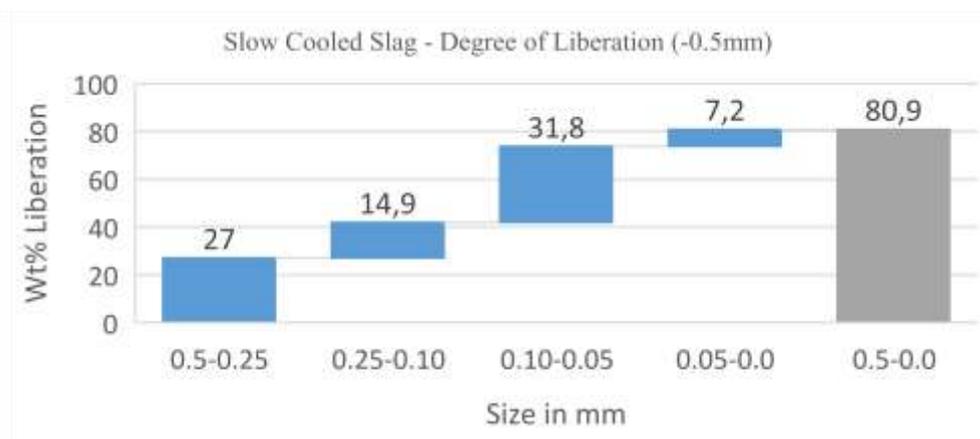


Figure 14 - Cumulative degree of liberation of slowly cooled slag at 0.5mm size

Conclusions

The present research work focused on developing enablers and characterization of material to develop a hybrid material containing both lime and iron oxide. The hybrid material is an excellent source of material for the iron and steel industry since it helps in easy melt formation during the process.

A research gap exists in the area of slag modification through control on cooling rate. In this process, any segregation in the elemental distribution of phases would result in the concentration of elements. Based on the characterization and detailed experimental studies and analysis of results, the following conclusions are drawn.

1. The as-received LD slag (also referred to as Normally cooled slag), which is cooled in 3 hours in industrial practice is different from the slowly cooled slag in respect to its crystal size and mineral liberation. The grain size of various grains in normally cooled slag was between 10-150 μm while the same for slowly cooled slag was 20-250 μm indicating that the slow cooling has resulted in grain growth and better liberation.

2. The liberation analysis indicated that at 0.5mm grind size the cumulative liberation of normally cooled slag was 69.2%, while 80.9%, for slowly cooled slag.

3. It was also shown that slow cooling promotes the formation of an additional phase which is essentially the dicalcium silicate phase (C_2S), with some amounts of FeO and MgO in the crystal lattice. This additional phase constituted about 6.2% in slowly cooled slag.

4. The results also confirm that with slow cooling, there is an increased concentration of phosphorus phase in calcium silicate phase C_2S and C_3S . The phosphorus concentration was up to 8% in slowly cooled slag against 5% in normally cooled slag.

Conflict of interests. On behalf of all authors, the correspondent author declares that there is no conflict of interests.

Acknowledgements. The authors thank the Research & Development Division and Management of Tata Steel Ltd. for their support and permission to publish this work. The authors also appreciate the resource and infrastructure support provided by CSIR-NML for conducting characterization and experimental studies. The authors would like to sincerely thank Scientists and faculty members of the Academy of Scientific and Innovative Research (AcSIR). The latter have provided valuable technical inputs for enriching the contents of this research work and helped the corresponding author complete the Doctoral Programme offered by AcSIR, Ghaziabad, India.

Cite this article as: Dilip M., Rajendra K.R. (2021). Modification of microstructure of LD slag for recovery of hybrid flux material. *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources*. Volume 4, Issue 319, pp. 81-93. <https://doi.org/10.31643/2021/6445.44>

Гибридті қождамалық материалды алу үшін ЛД-қождың микроқұрылымын модификациялау

^{1,3}Дилип М., ^{1,2}Раджендра К.Р.

¹Ғылыми -инновациялық зерттеулер академиясы, Газиабад, Үндістан

²CSIR-Ұлттық металлургия зертханасы, Джамшедпур, Үндістан

³Зерттеу және әзірлеу бөлімі, Tata Steel Ltd, Джамшедпур, Үндістан

Мақала келді: 03 тамыз 2021

Сараптамадан өтті: 26 қыркүйек 2021

Қабылданды: 26 қазан 2021

ТҮЙІНДЕМЕ

Болат өндіру процесінде оттегі пешінде шығымы шамамен 125 кг / т болатын конвертерлік қож (ЛД- қож) түзіледі. ЛД-қож құрамындағы вюстит пен екі кальцийлі ферритте шамамен 18% Fe және шамамен 45% CaO бар. Бұл минералдар болат өнеркәсібі үшін балама қождамалардың (флюстердің) тамаша көзі болып табылады. Қожды модификациялау және терең зерттеулер арқылы балама қождамалық материал ретінде қолдануға болатын материалды әзірлеу бойынша зерттеулер жүргізілді. Кристалл құрылымының, фазалық таралудың, түйіршіктердің мөлшерінің өзгеруін анықтау үшін SEM-EPMA және XRD көмегімен сипаттамаларға егжей-тегжейлі зерттеу жүргізілді. Фазалардағы түйіршіктердің мөлшері қалыпты салқындатылған қож үшін 10 -нан 150 мкм -ге дейін және баяу салқындатылатын қож үшін 20 -дан 250 мкм -ге дейін болатындығы анықталды. Баяу салқындату кристалдық торда FeO мен MgO-ның белгілі мөлшерлері бар екі кальцийлі силикат фазасы болып табылатын қосымша фазаның пайда болуына ықпал ететіні де көрсетілді. Жалпы алғанда, ЛД-қожының шамамен 50% -ы шамамен 30% CaO және 30% Fe бар балама қождамалық материал ретінде алынуы мүмкін екендігі айтылады. Бұл балама қождама балқу температурасы төмен қож түзуіне байланысты болат өнеркәсібінде қолдануға арналған тамаша материал көзі болып табылады.

Түйін сөздер: ЛД-қож, сипаттама, гибридті қождама (флюс), салқындату жылдамдығы, микроқұрылым.

Авторлар туралы ақпарат:

Докторант, Ғылыми-инновациялық зерттеулер академиясы, Газиабад-201002, Үндістан; Зерттеу және әзірлеу бөлімі, Tata Steel Ltd, Джамшедпур, Үндістан. E-mail: dmakhija14@gmail.com, <https://orcid.org/0000-0002-5011-2671>

Дилип Махиджа

Раджендра Кумар Рат

Аға ғылыми қызметкер, CSIR Ұлттық металлургия зертханасы, пайдалы қазбаларды өңдеу бөлімі, Джамшедпур, 831007, Үндістан; Ғылыми -инновациялық зерттеулер академиясы, Газиабад, Үндістан. E-mail: rkrath@nmlindia.org

Модификация микроструктуры ЛД-шлака для получения гибридного флюсового материала

^{1,3}Дилип М., ^{1,2}Раджендра К.Р.

¹Академия научных и инновационных исследований, Газиабад, Индия

²CSIR-Национальная металлургическая лаборатория, Джамшедпур, Индия

³Подразделение исследований и разработок, Tata Steel Ltd, Джамшедпур, Индия

АННОТАЦИЯ

В процессе производства стали в кислородной печи образуется конвертерный шлак (ЛД-шлак) с расходом около 125 кг/т. ЛД-шлак содержит около 18% Fe в вюстите и двухкальциевом феррите и около 45% CaO. Эти минералы являются отличным источником альтернативных флюсов для сталелитейной промышленности. Посредством модификации шлака и углубленных исследований, были проведены обследования для разработки материала, который можно было бы использовать в качестве альтернативного флюсового материала. Подробные исследования характеристик были проведены с использованием SEM-EPMA и XRD для выявления изменений в кристаллической структуре, фазовом распределении, размере зерен. Было обнаружено, что размер зерна фаз составляет от 10 до 150 мкм для нормально охлаждаемого шлака и от 20 до 250 мкм для медленно

Поступила: 03 августа 2021

Рецензирование: 26 сентября 2021

Принята в печать: 26 октября 2021

охлаждаемого шлака. Также показано, что медленное охлаждение способствует образованию дополнительной фазы, которая по существу представляет собой фазу двухкальциевого силиката с некоторыми количествами FeO и MgO в кристаллической решетке. В целом отмечено, что около 50% ЛД-шлака может быть извлечено в качестве альтернативного флюсового материала, содержащего примерно 30% CaO и 30% Fe. Этот альтернативный флюс из-за образования шлаков с низкой температурой плавления является отличным источником материала для использования в сталелитейной промышленности.

Ключевые слова: ЛД-шлак, характеристика, гибридный флюс, скорость охлаждения, микроструктура.

Дилип Махиджа	Информация об авторах: Докторант, Академия научных и инновационных исследований, Газиабад, 201002, Индия; Подразделение исследований и разработок, Tata Steel Ltd, Джамшедпур, Индия. Email: dmakhija14@gmail.com, https://orcid.org/0000-0002-5011-2671
Раджендра Кумар Рат	Старший научный сотрудник отдела переработки полезных ископаемых, CSIR-Национальная металлургическая лаборатория, Джамшедпур, 831007, Индия; Академия научных и инновационных исследований, Газиабад, Индия. Email: rkrath@nmlindia.org

Reference

- [1] Tleugabulov S.M., Aitkenov N.B., Zhabalova G.G., Belichko A.G. and Uleva G. A, Metallurgical processing of converter slag, *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources*. Volume 3, Issue 318, 2021. <https://doi.org/10.31643/2021/6445.26>
- [2] I.Z. Yildirim and M. Prezzi, Chemical, mineralogical, and morphological properties of steel slag, *Adv. Civ. Eng.*, 2011(2011), Art. No. 463638.
- [3] X.R. Wu, G.M. Yang, L.S. Li, H.H. Lü, Z.J. Wu, and X.M. Shen. Wet magnetic separation of phosphorus containing phase from modified BOF slag, *Ironmaking Steelmaking*, 41(2014), p. 335.
- [4] B. Das, S. Prakash, P.S.R. Reddy, and V.N. Misra, An over-view of utilization of slag and sludge from steel industries, *Resour. Conserv. Recycl.*, 50(2007), p. 40.
- [5] N. Menad, N. Kanari, and M. Save, Recovery of high grade iron compounds from LD slag by enhanced magnetic separation techniques, *Int. J. Miner. Process.*, 126(2014), p. 1.
- [6] S. Radosavljevic, D. Milic, and M. Gavrilovski, Mineral processing of a converter slag and its use in iron ore sintering, *Magn. Electr. Sep.*, 7(1996), No. 4, p. 201.
- [7] J. Geiseler, Use of steelworks slag in Europe, *Waste Manage.*, 16(1996), No. 1-3, p. 59.
- [8] Sariyev O.R., Musabekov Z.B., Dossekenov M.S., Disposal of slag of refined ferrochromium by obtaining a sintered and carbonized construction product, *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources*, No.4, 2019. <https://doi.org/10.31643/2019/6445.35>
- [9] V. Ghai and W.H. Noseworthy, Resource recovery programs at Lake Erie Steel, *Iron Steel Eng.*, 1998, 75(5), p. 24.
- [10] L.S. Ökvist, D.Q. Cang, Y.B. Zong, and H. Bai, The effect of BCF slag and BF flue dust on coal combustion efficiency, *ISIJ Int.*, 44(2004), No. 9, p. 1501.
- [11] Bobrov V. M, Sit'ko E.A., Shamgunov A.S. and Kamirdinov A.G, Copper-smelting production's silicate-limy ores and slags fluxing ability and its influence on copper content in slags, *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources*, No.2, 2010
- [12] R. Panda, R.N. Karand, and C.R. Panda, Dephosphorization of LD slag by Penicillium citrinum, *The Ecoscan*, III (2013), Spec. Iss., p. 247.
- [13] P. Chaurand, J. Rose, V. Briois, L. Olivi, J. Hazemann, O. Proux, J. Domas, and J. Bottero, Environmental impacts of steel slag reused in road construction: a crystallographic and molecular (XANES) approach, *J. Hazard. Mater.*, 139(2007), No. 3, p. 537.
- [14] Y. Topkaya, N. Sevinç, and A. Günaydin, Slag treatment at Kardemir integrated iron and steel works, *Int. J. Miner. Process.*, 74(2004), No. 1-4, p. 31.
- [15] H. Nashiwa, T. Mizuno, J. Ohi, and K. Katohgi, Effective use of returned LD slag and dolomite and operation with sub lance system, *Ironmaking Steelmaking*, 5(1978), p. 95.
- [16] W.B. Dai, Y. Li, D.Q. Cang, Y.Y. Zhou, and Y. Fan, Effects of sintering atmosphere on the physical and mechanical properties of modified BOF slag glass, *Int. J. Miner. Metall. Mater.*, 21(2014), No. 5, p. 494.
- [17] K.K. Sharma, S. Swaroop, and D.S. Thakur, Recycling of LD slag through sinter route on direct charging in blast furnace at BHP Steel Plant, [in] *Proceedings of National Seminar on Pollution Control in Steel Industries*, Ranchi, 1993, p. 72.
- [18] K. Morita, M.X. Guo, N. Oka, and N. Sano, Resurrection of the iron and phosphorus resource in steelmaking slag, *J. Mater. Cycles Waste Manage.*, 4(2002), p. 93.
- [19] S.M. Jung and Y.J. Do, Reduction behaviour of BOF slag by carbon in iron, *Steel Res. Int.*, 77 (2006), p. 312.
- [20] S.H. Huang, Y.Q. Wu, X.S. Liu, Z.R. Xu, and X.H. Lv, Experimental study on gasification dephosphorization of converter slag with reduction by silicon, *Iron Steel*, 43(2008), No.2, p. 31.
- [21] H. Ono, A. Inagaki, T. Masui, H. Narita, T. Mitsuo, S. Nosaka, and S. Gohda, Removal of phosphorus from LD converter slag by floating of dicalcium silicate during solidification, *Tetsu-to-Hagane*, 66(1980), No. 9, p. 1317.
- [22] K. Yokoyama, H. Kubo, K. Mori, H. Okada, S. Takeuchi, and T. Nagasaka, Separation and recovery of phosphorus from steelmaking slags with the aid of a strong magnetic field, *ISIJ Int.*, 47(2007), No. 10, p. 1541.

- [23] H. Kubo, K.M. Yokoyama, and T. Nagasaka, Magnetic separation of phosphorus enriched phase from multiphase dephosphorization slag, *ISIJ Int.*, 50(2010), No. 1, p. 59.
- [24] F.J. Doucet, Effective CO₂-specific sequestration capacity of steel slags and variability in their behaviour in view of industrial mineral carbonation, *Miner. Eng.*, 23(2010), No. 3, p. 262.
- [25] Wang D., Jiang M., Liu C., Min Y., Cui Y., Liu J., and Zhang Y., "Enrichment of Fe-containing Phases and Recovery of Iron and Its Oxides by Magnetic Separation from BOF Slags." *Steel Research International*. vol. 82, no. 2. pp. 189–196. 2012.
- [26] Radosavljevic S., Milic D., and Gavrilovski M., "Mineral processing of a converter slag and its use in iron ore sintering", *Magnetic and Electrical Separation.*, 7(1996), No. 4, p. 201.
- [27] Svoboda, "Magnetic techniques for the treatment of materials" *Earth Sciences and geography*, 2004.
- [28] E.F. Wu, S. Pignolet-Brandom, and I. Iwasaki, Liberation analysis of slow cooled steel making slags: implications for phosphorus removal, *Proceedings of the 1st International Conference on Processing Materials for Properties*, Hono- lulu, 1993, p. 153.