ARCHIVES OF METALLURGY
Volume 48 2003 Issue 2

MAREK DZIARMAGOWSKI *

ASSESSMENT OF PROPERTIES OF NON-METALLIC PHASE OBTAINED DURING THE CONVERTER SLAG REDUCTION PROCESS

OCENA WŁASNOŚCI FAZY NIEMETALICZNEJ OTRZYMANEJ W PROCESIE REDUKCJI ŻUŻLA KONWERTOROWEGO

Investigation of the converter slag reduction process in electric arc furnace have been carried out for several years. The aim of the investigations is to obtain the non-metallic phase in the form of the Portland clinker. In the investigations presented, the conditions are determined under which obtaining the non-metallic phase as the Portland clinker is possible.

Badania procesu redukcji żużla konwertorowego w elektrycznym piecu łukowym prowadzone są w świecie od szeregu lat. Celem prowadzonych badań jest otrzymanie fazy niemetalicznej w postaci klinkieru portlandzkiego. W prezentowanych badaniach określono warunki, w których możliwe jest otrzymanie fazy niemetalicznej w postaci klinkieru portlandzkiego.

1. Introduction

Investigations of the converter slag reduction process have been carried out for several years under laboratory and semi-industrial conditions [1, 2]. Reduction in electric arc furnace produces metal and non-metallic phases. The aim of the investigations is to obtain the non-metallic phase in the form of the Portland clinker.

The non-metallic phase obtained in the form of the Portland clinker should contain 63% of CaO and less than 5% of MgO. Additionally, this phase should contain a $2CaO{\cdot}SiO_2$ form called colloquially belite in the cement chemistry or, mineralogically, larnite, which possesses hydraulic binding properties.

Determining conditions under which obtaining the non-metallic phase as the Portland clinker is possible is the aim of the investigations presented.

* WYDZIAŁ METALURGII I INŻYNIERII MATERIAŁOWEJ, AKADEMIA GÓRNICZO-HUTNICZA, 30-059 KRAKÓW, AL. MICKIEWICZA 30

2. Conditions for converter slag reduction depending on the non-metallic phase destination

The conditions that a non-metallic phase for Portland clinker production has to met show that the process should be run so as to obtain a stabilized phase which does not self-decompose. It was found in earlier investigations [3] that when a reducer amount (ground electrode) not exceeding 4% was applied then the slag reduction did not exceed 21% and the P_2O_5 content in the non-metallic phase exceeded 0.8% (more than 0.3% mol.), which permits the stabilized phase to be obtained. In melts operated with 5% reducer fraction, the reduction ratios increased to over 22% and at the same time the P_2O_5 content in the non-metallic phase did not exceed 0.4% (less than 0.2% mol.). The non-metallic phase obtained from these melts self-decomposed because of transformation of a β 2CaO SiO_2 form into a γ form. The results obtained were consistent with the results of other investigations [4, 5] stating that when the P_2O_5 content exceeds 0.3% mol. then calcium orthophosphate 2CaO SiO_2 stabilizes and the self-decomposition of non-metallic phase does not take place.

During chemical composition analysis of the non-metallic phase obtained from melts operated with reducer fraction not exceeding 4%, account was paid on the MgO content of 5.19% that was greater than the amount admissible in the Portland clinker. The average content of CaO was 61.50% and was smaller than the amount required in the clinker.

It follows from the investigations made that the obtained non-metallic phase can be utilized as the Portland clinker only when an additive of CaO is introduced to change the mineralogical composition so that the fraction of alite 3CaO SiO_2 increases and the fraction of belite 2CaO SiO_2 decreases.

3. Assessment of non-metallic phase chemical and mineralogical composition

The investigations were carried out in a single-electrode arc furnace. In testing melts, the ground Bessemer slag mixed with ground electrode and calcium oxide was used. The mass of the slag was 1000 g, of the reducer: 40 g, and of the calcium oxide: 10 g, 20 g, 50 g, 60 g and 70 g. The slag mixed with the reducer and calcium oxide was added in small portions to the melting pot for six minutes. After two minutes from the moment the slag adding ended, e.g., after eight minutes of the process duration, foaming of the mixture introduced to the graphite pot ended. In that period, the working current was 600 A and voltage 40 V. After the end of slag foaming, the process was run for one minute. Three melts were made for each lime additive amount.

The results of the tested chemical composition of the modified non-metallic phase and metallic phase obtained simultaneously are presented in Tables 1 and 2.

TABLE 1

Chemical composition of non-metallic phase, %

Melt no.	CaO mass [g]	Phase mass [g]	Chemical composition, %										
			C	CaO_C	CaO_w	SiO_2	MgO	FeO	MnO	Cr_2O_3	Al_2O_3	P_2O_5	ΣS
converter slag	-	10000.0	-	44.50	1.68	16.63	5.26	23.25	5.40	0.16	1.68	1.24	0.11
1–3	-	561.1	0.27	61.50	1.82	23.21	5.19	3.01	4.13	-	1.40	0.83	0.12
4–5	10	559.5	0.28	61.96	2.55	22.78	4.53	3.20	3.78	-	2.42	0.78	0.14
6–7	20	568.0	0.28	62.63	2.55	22.28	2.91	4.51	3.78	-	1.96	0.74	0.12
8–9	50	672.0	0.30	60.63	2.22	21.74	1.64	6.49	5.45	-	1.53	1.19	0.16
10–11	60	680.5	0.32	59.14	1.88	20.68	1.65	9.21	5.20	-	1.33	1.23	0.15
12–13	70	705.0	0.32	57.97	1.83	20.40	1.98	10.33	5.03	-	2.16	1.31	0.17

TABLE 2

Chemical composition of metallic phase, %

Melt no.	CaO mass [g]	Phase mass [g]	Chemical composition, %							
			C	Fe	Si	Mn	Al	Cr	P	ΣS
1–3	-	165.71	0.93	94.37	0.04	3.06	0.005	0.42	1.04	0.019
4–5	10	166.5	0.56	95.30	0.04	2.27	0.005	0.17	1.14	0.019
6–7	20	161.0	0.54	96.23	0.05	1.92	0.005	0.14	1.04	0.018
8–9	50	104.8	0.60	98.20	0.04	0.74	0.005	0.09	0.09	0.016
10–11	60	103.5	0.60	98.20	0.05	0.69	0.005	0.05	0.09	0.016
12–13	70	101.5	0.62	98.68	0.04	0.69	0.005	0.02	0.08	0.016

Based on these results, the converter slag reduction ratios was calculated and presented in Table 3. The reduction ratios was calculated according to the formula:

$$R_x = \frac{\Delta m_O}{m_O^{slag} - \Delta m_O^{loss}} \times 100, \quad (1)$$

R_x = reduction ratio of component x,
Δm_O = oxygen mass decrease in oxide of reduced component x,
m_O^{slag} = oxygen mass in oxide of reduced component x in converter slag,
Δm_O^{loss} = oxygen mass decrease in oxide of reduced component x owing to losses.

TABLE 3

Reduction ratios of slag componnt %

Melt no.	CaO mass [g]	Reduction ratios of slag component, %					
		Fe	Si	Mn	Al	P	R_{slag}
1–3	–	92.25	0.13	22.03	0.20	45.88	21.10
4–5	10	91.94	0.13	18.75	0.12	49.91	21.19
6–7	20	88.61	0.16	15.68	0.14	47.72	20.60
8–9	50	75.22	0.07	2.66	0.10	2.63	12.21
10–11	60	67.59	0.09	2.54	0.11	2.49	12.01
12–13	70	63.89	0.07	2.48	0.06	1.98	11.39

The changes in the chemical composition of the non-metallic phase and metallic phase presented in Tables 1 and 2 suggest that a small amount of the of CaO additive of 1-2% of the converter slag mass does not affect significantly the slag reduction ratios. The content of CaO in the obtained non-metallic phase increases by 0.5-1.0%. At the same time, the SiO2 content decreases by 0.5-1.0% which is favourable regarding the clinker chemical composition. Moreover, the MgO content decreases to below 5%, which also is favourable regarding the clinker composition.

Decreasing of the MgO content follows probably from the fact that the CaO additive results in a rise of the slag melting temperature, then the slag becomes denser, which permits work at the practically enclosed arc. Under those conditions, melt losses decrease and the temperature in the arc impact zone increases. This can affect the MgO dissociation increase and evaporation of magnesium. This phenomenon confirms an increase of losses of magnesium and chromium.

Increasing CaO additive amount to a 5-7% of the converter slag mass should be considered as purposeless because of the process rate decrease caused by a slag melting temperature increase. In such a case, higher slag reduction ratios requires a substantial extension of process duration.

The mineralogical composition of the obtained non-metallic phase was determined by *X*-ray crystallography analysis. The results given in Table 4 showed that the crystals of alite

$3CaO\ SiO_2$ and belite (larnite) $2CaO\ SiO_2$ constitute its basic part. Comparing the obtained mineralogical composition with the composition of the phase obtained without CaO addition, it was found an increase of the alite fraction and decrease of that of belite. Moreover, the alite fraction was higher than the belite fraction. The latter was higher in the non-metallic phase without CaO addition. This means that an addition of CaO of 1-2% of the slag mass permits such modification of the mineralogical composition of the produced non-metallic phase that it meets the Portland clinker mineralogical requirements.

TABLE 4

Mineralogical composition of Portland clinker and non-metallic phase

Portland clinker			Non-metallic phase obtained without CaO addition			Non-metallic phase obtained with the 20 g CaO addition		
d(Å)	I/I_{max}	Phase	d(Å)	I/I_{max}	Phase	d(Å)	I/I_{max}	Phas
5.90	3	C_3S	5.92	1.5	C_3S	5.910	1	C_3S
5.45	3	C_3S	-	-	-	5.470	1	C_3S
3.031	7	C_3S	3.017	3.5	C_3S	3.020	4	C_3S
2.963	3	C_3S	2.961	1	C_3S	2.957	1.5	C_3S
2.877	1	C_2S	2.877	0.5	C_2S	2.875	0.5	C_2S
2.813	3	C_2S	2.810	0.5	C_2S	2.813	1	C_2S
2.777	10	$C_3S + C_2S$	2.779	10	$C_2S + C_2S$	2.775	10	$C_3S + C_2S$
2.747	9	C_2S	2.743	4	C_2S	2.747	5	C_2S
2.735	6	C_3S	2.733	5	C_3S	2.737	7	C_3S
2.700	6-1	C_3A	-	-	-	-	-	-
2.660	5-1	C_4AF	-	-	-	-	-	-
2.605	8	C_3S	2.603	4	C_3S	2.599	5	C_3S
2.442	2	C_2S	-	-	-	2.438	1	C_2S
-	-	-	-	-	-	2.401	0.5	C
2.308	2	$C_3S + C_2S$	2.3120	2	$C_2S + C_2S$	2.3117	1.5	$C_3S + C_2S$
2.283	2	C_2S	2.2800	1	C_2S	2.2802	0.5	C_2S
2.182	6	$C_2S + C_3S$	2.1782	2	$C_2S + C_3S$	2.1789	3	$C_3S + C_2S$
2.165	7	C_3S	2.1592	1.5	C_3S	2.1610	2	C_3S
2.089	2	$C_2S + C_3S$	-	-	-	2.0886	0.5	$C_3S + C_2S$
2.052	2	$C_2S + C_3S$	-	-	-	2.0482	0.5	$C_3S + C_2S$
2.021	2	$C_2S + C_3S$	-	-	-	2.0179	0.5	$C_3S + C_2S$
1.975	2	C_3S	1.9729	1	C_3S	1.9754	1	C_3S
1.930	2	C_3S	1.9297	1	C_3S	1.9302	1	C_3S
1.802	2	$C_2S + C_3S$	1.8240	0.5	$C_2S + C_3S$	1.8241	0.5	$C_3S + C_2S$
1.760	1	C_3S	1.7602	2	C_3S	1.7598	2	C_3S

C – CaO, S – SiO_2 A – Al_2O_3 F – Fe_2O_3

4. Assessment of properties of non-metallic phase

In order to assess the suitability of the obtained non-metallic phase for Portland clinker production, calculations were made of hydraulic module, M_h, alkalinity module, M_z, and activity module, M_a, defined as follows:

$$M_h = \frac{\%CaO}{\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3}$$

$$M_z = \frac{\%CaO + \%MgO}{\%SiO_2 + \%Al_2O_3 + \%MnO} \tag{2}$$

$$M_a = \frac{\%CaO + \%MgO + \%Al_2O_3}{\%SiO_2 + \%MnO}.$$

Magnitudes of the modules calculated for the obtained phase are presented in Table 5. The calculated results show that high alkalinity and activity and high hydraulic module are the features of the obtained non-metallic phase.

TABLE 5

Magnitudes of modules calculated: hydraulic, alkalinity and activity modules

Melt no.	CaO mass [g]	Modules		
		M_h	M_z	M_a
1–3	-	2.49	2.32	2.49
4–5	10	2.46	2.30	2.60
6–7	20	2.56	2.34	2.59
8–9	50	2.51	2.17	2.35
10–11	60	2.57	2.24	2.34
12–13	70	2.48	2.18	2.45

Taking into account both chemical and mineralogical composition of non-metallic phase obtained with 4% reducer fraction, it can be stated that this material can be utilised as:

- Portland clinker,
- additive to the joint milling with Portland clinker for cement,
- binder replacing cement in production of cellular concretes,
- a part of the binder replacing lime in production of lime-sand bricks,
- binder in production of colour plaster materials.

Heavy metal compounds contained in the non-metallic phase chemical composition do not interfere with any of the technologies mentioned above.

5. Conclusions

1. Stabilized non-metallic phase can be obtained in the converter slag reduction process in an electric arc.

2. Stabilized non-metallic phase can be obtained at the 4% reducer fraction. The slag reduction ratios is then about 21% and the P_2O_5 content in the non-metallic phase is not less than 0.8% (0.3% mol.).
3. The obtained non-metallic phase can be used as a Portland clinker after adding a CaO additive to obtain changes in mineralogical composition consisting in increased fraction of alite $3CaO\ SiO_2$ and decreased fraction of belite $2CaO\ SiO_2$.
4. Mineralogical composition can be changed by reducing a mixture of converter slag, reducing agent and pure CaO. Addition of CaO amounting to 1-2% of the converter slag mass permits such modification of the non-metallic phase mineralogical composition that it meets the Portland clinker mineralogical requirements.
5. High alkalinity and activity and high hydraulic module are the features of the obtained modified non-metallic phase.

REFERENCES

[1] S. Kubodera, T. Koyama, R. Ando, R. Kondo, Transactions of The Iron and Steel Institute of Japan **19**, 7, 419–427 (1979).

[2] J. Piret, A. Dralants, Stahl und Eisen **104**, 16, 774–778 (1984).

[3] M. Dziarmagowski, M. Karbowniczek, M. Pyzalski, J. Okoń, Ironmaking and Steelmaking **1**, 45–49 (1992).

[4] E. Duczymińska, Stabilizacja fazy krzemianu dwuwapniowego, AGH Kraków 1967.

[5] A. Derdacka-Grzymek, Polska Akademia Nauk, Prace Komisji Ceramicznej, Ceramika **31**, 161–154 (1981).

REVIEWED BY: ANDRZEJ ŁĘDZKI

Received: 7 January 2003.