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RESEARCH ON OPPORTUNITIES OF MODIFICATION OF CHEMICAL COMPOSITION OF THE NON-METALLIC PHASE OBTAINED IN THE CONVERTER SLAG REDUCTION PROCESS

BADANIA MOŻLIWOŚCI MODYFIKACJI SKŁADU CHEMICZNEGO FAZY NIEMETALICZNEJ OTRZYMYWANEJ W PROCESIE REDUKCJI ŻUŻŁA KONWERTOROWEGO

The objective of the performed tests was to determine opportunities of modification of chemical composition of the non-metallic phase obtained in the process of converter slag reduction in an electric arc furnace. The obtained phase can be used as Portland cement clinker only after adjustment of its chemical and mineralogical composition. The adjustment was performed during the reduction process by means of various CaO additions to the charge. The performed tests enabled to find that along with an increase in the CaO addition to the charge, the CaO content in the chemical composition and the $3\text{CaO}\cdot\text{SiO}_2$ -alite content in the mineralogical composition of the obtained non-metallic phase increased. By adding adequate CaO additions to the charge it was possible to obtain a phase with its chemical and mineralogical composition meeting the requirements set for Portland cement clinker. It was also found that too much of CaO in the charge caused increase in the melting temperature of the mixture and slowed the reduction process down.

Celem przeprowadzonych badań było określenie możliwości modyfikacji składu chemicznego fazy niemetalicznej otrzymywanej w czasie procesu redukcji żużła konwertorowego w elektrycznym piecu łukowym. Otrzymywana faza może zostać wykorzystana jako klinkier portlandzki dopiero po korekcie jej składu chemicznego i mineralogicznego. Korektę przeprowadzono w czasie procesu redukcji stosując różne dodatki CaO do wsadu. Przeprowadzone badania pozwoliły na stwierdzenie, że ze wzrostem dodatku CaO do wsadu następuje wzrost udziału CaO w składzie chemicznym i wzrost udziału $3\text{CaO}\cdot\text{SiO}_2$ — alitu w składzie mineralogicznym otrzymywanej fazy niemetalicznej. Stosując odpowiednie dodatki CaO do wsadu można otrzymać fazę o składzie chemicznym i mineralogicznym spełniającym wymogi stawiane dla klinkieru portlandzkiego. Stwierdzono również, że zbyt duży dodatek CaO do wsadu powoduje wzrost temperatury topnienia mieszaniny i spowolnienie procesu redukcji.

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1. Introduction

Research on the converter slag reduction process in an electric arc furnace carried out for many years can fall within new methods of converter slag utilization. As a result of the process a metallic and a non-metallic phase can be obtained, which can be utilized for Portland cement clinker manufacturing or as a Ca-Mg fertilizer.[1-3].

The non-metallic phase obtained can be utilised as Portland cement clinker only after adjustment of its composition, which consists in increase in CaO content in its chemical composition and increase in $3\text{CaO}\cdot\text{SiO}_2$ -alite content in its mineralogical composition. There have been trials of chemical composition adjustment after obtaining the non-metallic phase in an electric arc furnace.[1]. No attempts to adjust the mineralogical composition have been mentioned in the available references. Also no research on possibilities of modification of the chemical and mineralogical composition of the non-metallic phase during the reduction process has been carried out. Therefore it has been decided to carry out tests in order to find out these opportunities.

2. Research methodology

Tests were performed in a single-electrode electric arc furnace. Ground converter slag blended with ground electrode and calcium oxide were used in experimental heats. The mass of slag was 1000g and the masses of calcium oxide were 10g, 20g, 50g, 60g and 70g. Slag blended with the reducing agent and calcium oxide would be added to the crucible in small portions during six minutes. After two minutes as of the end of slag feeding, foaming of the mixture would end. Three heats were made for each lime addition.

The test results of the chemical composition of the converter slag and the obtained non-metallic phase are presented in Table 1. The mineralogical composition was determined by XRD method. The test results are presented in Table 2 and Fig. 1-4.

TABLE 1
Chemical composition of non-metallic phase, %

No.	CaO mass [g]	Phase mass [g]	Chemical composition, %				
			CaO	SiO ₂	MgO	FeO	MnO
converter slag	—	10000,0	44,50	16,63	5,26	23,25	5,40
1	—	561,1	61,50	13,21	5,19	3,01	4,13
2	10	559,5	61,96	22,78	4,53	3,20	3,78
3	20	568,0	62,63	22,28	2,91	4,51	3,78
4	50	672,0	60,63	21,74	1,64	6,49	5,45
5	60	680,5	59,14	20,68	1,65	9,21	5,20
6	70	705,0	57,97	20,40	1,98	10,33	5,03

TABLE 2

The test results of XRD phase analysis

No.	CaO addition, %																				
	0			1			2			5			6			7					
	d_{hkl}	I/Im %	Phases	d_{hkl}	I/Im %	Phases	d_{hkl}	I/Im %	Phases	d_{hkl}	I/Im %	Phases	d_{hkl}	I/Im %	Phases	d_{hkl}	I/Im %	Phases			
1	3.86	3	CS, C2S	3.859	4	CS, C3SS	3.857	3	C3S	3.88	4	C2S, C3S	3.84	5	C3S, C2S, F	3.875	4	C3S, C2S			
2	3.509	2	CS, C3S	3.493	4	CS, C3SS	3.531	3	C3S	3.523	4	C3S	3.194	3	C3S, C2S	3.521	4	C3S			
3	3.195	3	C3S, C2S				3.186	4	C3S, C2S	3.19	6	C3S, C2S	3.194	3	C3S, C2S	3.194	4	C3S, C2S			
4	3.029	31	C3S, C2S	3.03	38	C3S, C2S	3.028	33	C3S, C2S	3.031	46	C3S, C2S	3.02	42	C3S, C2S	3.031	63	C3S, C2S			
5	2.959	9	C2S, C3S	2.955	9	C2S, C3S	2.965	12	C3S, C2S	2.966	15	C3S, C2S	2.957	9	C3S, C2S	2.958	13	C3S, C2S			
6	2.877	2	C2S, C3S	2.876	4	C2S, C3S2	2.879	3	C2S, C3S	2.88	4	C3S, C2S	2.876	5	C2S, C3S	2.876	4	C3S, C2S			
7	2.772	100	C3S, C2S	2.774	100	C2S, C3S	2.776	100	C3S, C2S	2.774	100	C3S, C2S	2.775	100	C3S, C2S	2.775	100	C3S, C2S			
8	2.736	41	C3S	2.734	59		2.748	57	C3S	2.745	60	C3S	2.737	59	C3S	2.736	73	C3S			
9	2.679	9	C3S	2.677	4	C3S	2.681	10	C3S				2.67	5	C3S						
10	2.599	40	C3S	2.595	45	C2S, C3S	2.611	57	C3S	2.606	54	C3S	2.6	41	C3S	2.6	64	C3S			
11	2.431	9	C4AF	2.434	5	C4AF	2.44	12	C4AF	2.496	8	C4AF	2.488	6	C4AF						
12										2.447	6	C4AF	2.436	8	C4AF, C3S	2.438	5	C4AF			
13										2.404	6	C4O	2.403	3	C4O	2.368	21	C4O			
14	2.314	9	C3S	2.313	7	C3S	2.315	13	C3S	2.322	8	C3S	2.312	11	C3S	2.31	11	C3S			
15	2.281	2	CS, C2S	2.283	4	CS, C2S	2.287	6	C3S, C2S	2.291	4	C3S	2.28	3	C3S, C2S						
16	2.176	22	CS	2.178	30	CS, C3S	2.181	10	C3S, C2S	2.185	38	C3 S, C2S	2.179	34	C3S, C2S	2.178	43	C3S, C2S			
17	2.159	7	C3S	2.151	13	C3S	2.164	36	C3S	2.167	27	C3S	2.161	22	C3S	2.16	18	C3S			
18	2.117	5	C2S	2.092	2	C2S	2.108	7	C2S	2.088	2	MgO	2.089	3	C2S, C3S						
19	1.973	3	C3S	1.973	5	C3S	1.975	4	C3S	1.979	6	C3S	1.975	5	C3S	1.975	7	C3S, C2S			
20	1.929	5	C4AF, C3S	1.929	5	C4AF, C3S	1.932	4	C3S, C4AF	1.934	10	C3S, C4AF	1.93	6	C3S, C4AF	1.93	9	C4AF, C3S			
21	1.898	3	C2S	1.898	4	C2S	1.891	3	C2S	1.907	2	C2S									
22	1.822	3	C3S	1.822	4	C3S	1.821	3	C3S	1.822	6	C3S	1.824	3	C3S	1.824	5	C3S			
23	1.762	16	C3S	1.761	23	C3S	1.763	22	C3S	1.761	31	C3S	1.761	7	C3S	1.761	27	C3S			
24	1.759	16	C3S													1.755	17	C3S			
25	1.692	3	C2S							1.694	3	C2S	1.696	3	C2S		5	C2S			
26	1.625	14	C3S	1.626	13	C3S	1.625	10	C3S	1.626	17	C3S	1.623	13	C3S	1.626	14	C3S			

CS - CaO-SiO₂, C2S - 2CaO-SiO₂, C3S - 3CaO-SiO₂, C4AF - 4CaO-Al₂O₃-Fe₂O₃

3. Assessment of the influence of CaO addition on the chemical and mineralogical composition of the non-metallic phase

The Portland cement clinker chemical composition is contained within the following limits: 63-67% CaO, 21-24% SiO₂, 4-7% Al₂O₃, 2- 4%FeO, max. 5% MgO and max. 1,5% SO₃. The mineralogical composition should be as follows: 40-70% 3CaO·Al₂O₃-alite, 15- 30% 2CaO·SiO₂-belite, 5-15% 3CaO·Al₂O₃, 5-15% 4CaO·Al₂O₃·Fe₂O₃ and max. 5% MgO- periclase. The obtained non-metallic phase can disintegrate autogenously, which occurs as a result of transformation of the β 2CaO variety into the γ variety. As a result of the transformation the volume increases and the non- metallic phase loses its hydraulic binding properties.

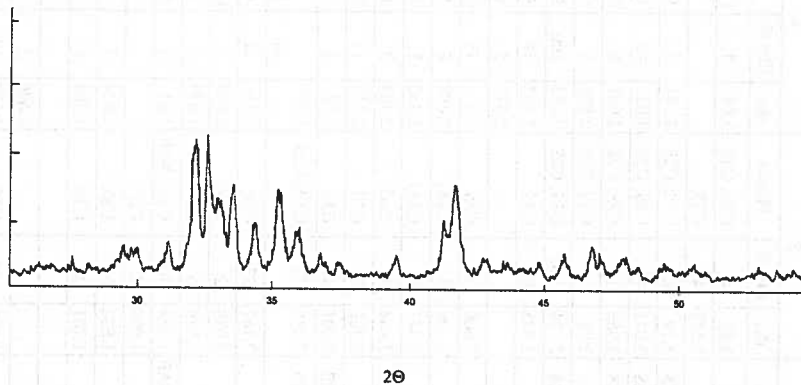


Fig. 1. Diffraction pattern of converter slag

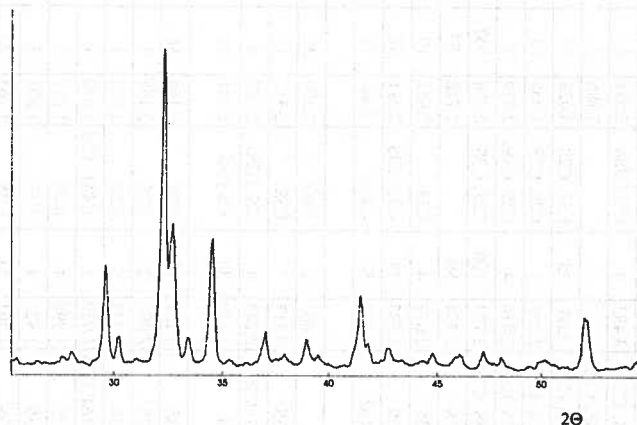


Fig. 2. Diffraction pattern of the non-phase obtained without CaO addition

Possibilities of the β 2CaOSiO₂ variety stabilization have been researched for many years. It has been found that stabilization of the β 2CaO·SiO₂ variety depends on its chemical composition and cooling conditions. The non-metallic phase not disintegrat-

ing autogenously can be obtained if the P_2O_5 content exceeds 0,3% molar concentration. If the P_2O_5 content is lower it is necessary to cool the obtained phase quickly. [4, 5]

Earlier research [6] has shown that a non-metallic phase not disintegrating autogenously can be obtained if the reducing agent content is 4%. In that case intensified cooling is not necessary and the obtained material can remain in the crucible. By reducing converter slag the CaO content obtained was lower than in Portland clinker while the MgO content slightly exceeded 5%. In addition the $2CaO \cdot SiO_2$ -belite content was higher than the $3CaO \cdot SiO_2$ -alite content. Therefore it was decided to modify the non-metallic phase chemical composition by addition of pure CaO to the charge.

The variations of the non-metallic chemical composition presented in Table 1 indicated that a small CaO addition of 1-2% of the converter slag mass caused increase in the CaO content in the obtained phase by 0.5-1,0%. At the same time the SiO_2 and MgO content decreased, which was beneficial for the clinker chemical composition.

Increase of the CaO addition to 5-7% of the converter slag mass turned out to be pointless because of a fall in the reduction process rate caused by an increase in the melting temperature. Under this circumstances FeO, MnO and P_2O_5 content in the obtained non-metallic phase increases. This causes reduction of the CaO content to the amount lower than required for the Portland clinker.

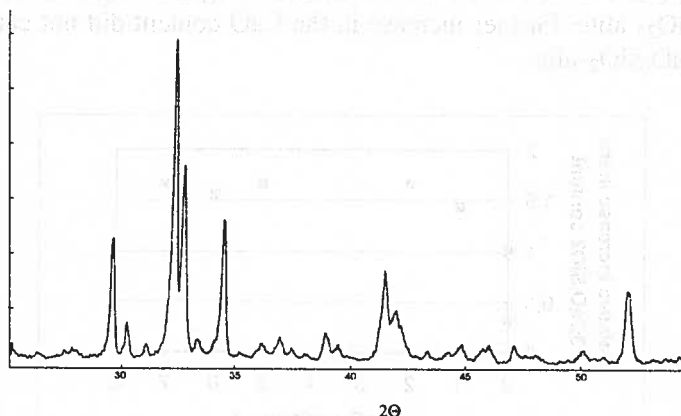


Fig. 3. Diffraction pattern of the non-metallic phase obtained without addition of 1% CaO

The mineralogical composition test results indicate that the basic part of the non-metallic phase comprises of: $3CaO \cdot SiO_2$ -alite and $2CaO \cdot SiO_2$ -belite. By comparing of the mineralogical composition of the non-metallic phase obtained without CaO addition with the mineralogical composition of the phases obtained with the CaO addition it was found that the $3CaO \cdot SiO_2$ -alite content increased and the $2CaO \cdot SiO_2$ - belite decreased. The $3CaO \cdot SiO_2$ -alite content was higher than the $2CaO \cdot SiO_2$ - belite content. In the non-metallic phase there is also $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ -browmillerite, $CaO \cdot SiO_2$ wollastonite and unreacted (free) calcium oxide CaO and magnesium oxide MgO.

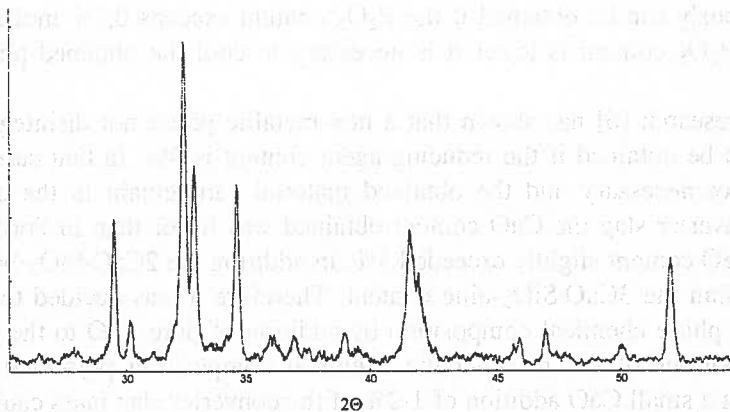


Fig. 4. Diffraction pattern of the non-phase obtained without addition of 5%CaO

Changes in the $3\text{CaO}\cdot\text{SiO}_2$ -alite content in relation to its content in the non-metallic phase obtained without the CaO addition are presented in Fig. 5. The results obtained indicate that in the non-metallic phase obtained without the CaO addition the $3\text{CaO}\cdot\text{SiO}_2$ -alite content was more than three times higher than in the converter slag. Increase in the CaO addition to 2% of the converter slag mass caused 1,7 times increase in the $3\text{CaO}\cdot\text{SiO}_2$ -alite. Further increase in the CaO content did not cause substantial changes in $3\text{CaO}\cdot\text{SiO}_2$ -alite.

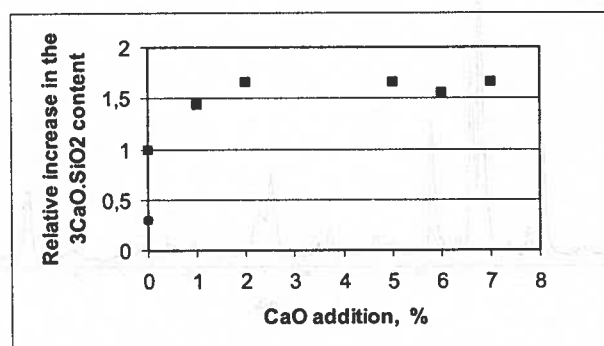


Fig. 5. Influence of CaO addition on increase in the $3\text{CaO}\cdot\text{SiO}_2$ content in the non-metallic phase

The performed tests indicate that CaO addition to the charge in the amount of up to 2% of the reduced slag mass enables to obtain the non-metallic phase of chemical and mineralogical composition very similar to the chemical composition of Portland cement clinker. To get comprehensive evaluation of the obtained phase it is necessary to perform tests of its binding properties. Also tests to determine the mass of CaO addition to the charge in relation to the chemical composition of the reduced converter slag should be carried out.

Selection of the method of modification of chemical and mineralogical composition of the obtained non-metallic phase should depend on the process costs. Introduction of CaO addition to the charge causes a sudden growth of the melting temperature, which affects increase of electricity consumption in the process and causes cost increase. It is not possible to estimate increase in energy consumption for the charge mass of 1 kg and a very small CaO addition. Assessment of electricity consumption require carrying out tests with much higher mass of the charge. Only when the problems presented are explained one can make decision on how to modify the chemical and mineralogical composition of the obtained non-metallic phase. Depending on the process costs the modification can be performed during the reduction process or after cooling and grinding the obtained phase. The option of partial modification of the composition during the reduction process and after completion of the process cannot be excluded.

4. Conclusions

Research on the converter slag reduction process in an electric arc furnace is carried out in the world for many years. The obtained non-metallic phase can be used as Portland cement clinker only after adjustment of its chemical composition. Modification of the chemical composition of the obtained phase is attempted after its production. There is no research on how the chemical composition adjustment influences the mineralogical composition.

The tests carried out enabled to find that modification of the chemical and mineralogical composition of the obtained non-metallic phase could be performed already during the reduction process. CaO should be added to the charge to obtain a higher CaO content in the chemical composition and an increase in the $3\text{CaO}\cdot\text{SiO}_2$ -alite content in the mineralogical composition. It was found that the CaO addition for the tested converter slag should not exceed 2% of the charge mass. If the additions were higher the melting temperature of the reduced mixture would increase and the reduction process would slow down.

The test results should be verified by carrying out reduction process of converter slag with various chemical compositions. It should enable to determine optimal CaO additions depending on the slag chemical composition.

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