VALORIFICAREA ŢUNDERELOR ÎN MATERIALE CU VALOARE ADĂUGATĂ
VALORIZATION OF MILL SCALES IN MATERIALS WITH ADDED VALUE

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The paper presents the results of laboratory research concerning the possibility of replacement the pyrite cinder from the clinker's raw mix, with other waste with high Fe_2O_3 content, like mill scale. An assessment of technological and qualitative aspects that involved this issue was taken into account. The influence of mill scale both on the raw mix burnability and clinker characteristics was investigated. The composition, mineralogical and structural – textural features of the resulted clinkers were characterised by wet chemistry, X-rays diffraction, and optical microscopy analysis. Also, theoretical consumption of heat at clinker formation was assessed. Cements CEM I were obtained from clinkers synthetised in the laboratory. These cements were characterized from physical-mechanical point of view, according to SR EN 197-1. The qualitative appreciations and the technological behavior were achieved in comparison with a raw mix, obtained from current raw materials, considered as reference. Presence of mill scale in raw mix did not modify qualitative characteristics of the clinker and cement, respectively. This finding sustains the possibility of replacement of the pyrite cinder with mill scale in clinker raw mix.

Lucrarea prezintă rezultatele cercetărilor de laborator privind posibilitatea înlocuirii cenuşii de pirită din amestecul brut la fabricarea clincherului, cu alt deşeu cu conținut ridicat de Fe_2O_3 – ţunder, precum şi evaluarea aspectelor tehnologice şi calitative care le implică. S-a investigat influența ţunderului asupra aptitudinii la clincherizare a amestecului brut şi a caracteristicilor clincherului. Clincherul a fost caracterizat din punct de vedere chimic, mineralogic și structural – textural prin analiza difractometrică cu raze X, microscopie optică. De asemenea, s-a estimat consumul teoretic de căldură la formarea clincherelor. Din clincherele obţinute s-au realizat, conform SR EN 197-1, cimenturi tip CEM I care au fost caracterizate din punct de vedere fizico-mecanic. Aprecierile calitative şi de comportare tehnnologică s-au efectuat comparativ cu un amestec brut, obținut din materii prime uzuale, considerat etalon. Prezenţa ţunderului în amestecul brut nu modifică caracteristicile calitative ale clincherului, respectiv ale cimentului, fapt care susţine posibilitatea înlocuirii cenuşii de pirită cu acest tip de material.

Keywords: *clinker, steel mill scale waste, cement*

1. Introduction

The chemical composition of the raw mix used for clinker manufacture is one of the main factors of which depends the formation of mineralogical constituents of clinker and implicitly, cement quality. In order to achieve chemical composition of clinker, besides the main raw materials (limestone, marl/clay) the additions for composition correction are also necessary, either for the content of SiO_2 or content of Fe_2O_3 [1,2].

In the Romanian cement plants, sand waste for the correction of SiO_2 content and pyrite cinder (a waste from sulphuric acid manufacturing) for the correction of Fe_2O_3 content are used. Currently, use of the pyrite cinder has become a problem due to closure the activity of chemical plants in which is generated this waste. This requires finding solutions for pyrite cinder replacement for another material that presents both an equivalent content of iron and technological properties (granulometry, clinker grindability and burnability) that allow its introduction in manufacturing process of cement.

The iron ores or waste resulted from iron and steel industry is used worldwide as additions with high content of iron. [3-6]. In our country, the byproducts resulted from iron and steel industry have been recently considered a viable alternative to the previously mentioned problem, the mill scale being part of such derivative materials category.

During the processing of steel, iron oxides on the surface of the metal are formed. These oxides, known as mill scale, occur during continuous casting, reheating, and hot rolling operations. The mill scale is removed by water sprays and often recycled by the steel plant. Mill scale that cannot be recycled by steel plants could be used by Portland cement plants as an iron source and in the obtaining of other building materials. On the other hand, mill scale is considered a rich iron source with minimum impurities [5, 7-15].

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In this paper are presented the results of laboratory research regarding the possibility to use the mill scale as correction additions in the raw mix for Portland cement clinker manufacture.

2. Materials and methods

In this study were used the following materials: limestone, marl, pyrite cinder, mill scale, and gypsum.

The chemical composition of materials was obtained by wet chemistry using the standardised method described in SR EN 196-2 [16]. The mill scale was also analyzed from the main physical characteristics point of view (volume weight and particle size distribution) [17,18].

Raw mixes proposed were achieved through simultaneous grinding of raw materials in a laboratory mill. The raw mixtures ground at a fineness expressed by residue on the sieve of 90μm (R_{009}) of about 10% were subjected to burning in a chamber kiln with gas at the maximum temperature of 1450°C, with maintaining of a 30 minutes plateau, followed by fast cooling in air.

The burnability was determined on all raw mixes achieved in the laboratory, through determination of free CaO content at different temperatures from 1300°C to 1450°C. In order to obtain supplementary data regarding burnability other parameters which characterized burnability were calculated (on basis of chemical analyses). This parameters are: burnability index (BI), refractory factor (RF), burnability factor (BF), burning temperature [2, 15, 19, 20].

Calculation formulas are defined in relation to chemical composition:

$$BI = \frac{\%C_3S}{\%C_3A + \%C_4AF};$$

$$RF = \frac{\%C_3S + 0.6\%C_3A - 0.61\%C_4AF}{1.12\%C_3A + 1.45\%C_4AF};$$

$$BF = S_k + 10M_{Si} - 3(MgO + Na_2O + K_2O);$$

$$T = 1300 + 4.51C_3S - 3.74C_3A - 12.6C_4AF$$

The theoretical heat consumption at clinker formation was calculated with Onoda formula [19]

$$Q = 4.89Al_2O_3 + 7.14\ CaO + 5.87\ MgO - 73$$

The obtained clinkers were characterized from chemical point of view by wet chemistry according to SR EN 196-2 [16]. The influence of mill scale addition on mineralogical and structural characteristics was also investigated, by X-rays diffraction analyses and optical microscopy on thin sections (OM). The X-ray diffraction (XRD) patterns of analysed materials were obtained using a DRON3 equipment with a CuKα radiation, a scanning interval 2θ between 9 and 68°, with a step of 0.1°. The clinker phases microstructure was observed through optical microscopy using a Carl Zeiss Jena polarising microscope. Quantitative estimation of clinker phases was obtained using visual comparision with percentage diagrams, method described by Campbell [21].

From the obtained clinkers were prepared cements, according to SR EN 197-1[22]. The cements were obtained by grinding the clinkers together with an addition of 5% gypsum, in a laboratory mill, up to a corresponding fineness of a Blaine specific surface area of about 3500cm^2/g. The cements were characterized from physical-mechanical point of view. Setting time and soundness were tested according to the standard SR EN 196-3 and the compressive strength were tested according to the standard SR EN 196-1 [23, 24].

3. Results and discussions

3.1. Materials characteristics

Limestone, marl and pyrite cinder and mill scale were used, with the chemical compositions presented in Table 1.

The absence of sulphur from sulphides and of SO_3 in the mill scale is noticeable; otherwise, the presence of these compounds could adversely influence the emissions from the technological process.

The content of heavy metal in the pyrite cinder and the mill scale is presented in Table 2.

The results of analyzed heavy metals reveal that mill scale has lower levels of heavy metals than pyrite cinder.

The mill scale was also analyzed from the main physical characteristics point of view, and the results are presented in Table 3.

The mill scale has particles situated below 25 mm, fact that excludes the crushing operation previous to its introduction in manufacturing flow of the cement. Also, it is remarked the fact that the highest percent in particle size distribution is represented by fine-grained particles, below 3 mm.

Table 1

The chemical characteristics of the raw materials / *Caracteristicile chimice ale materiilor prime*

Raw material *Materia primă*	Characteristic/*Caracteristica* (%)									
	LOI/PC	CaO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	SO_3	Ss*
Limestone/*Calcar*	41.65	51.91	2.88	1.53	0.80	1.17	0.07	0.59	0.05	-
Marl / *Marnă*	19.18	21.27	37.57	9.40	5.17	1.00	2.46	2.23	0.06	-
Pyrite cinder *Cenușă de pirită*	2.50	6.26	9.61	2.11	73.32	1.65	0.50	0.50	3.43	2.26
Mill scale/*Țunder*	0.26	1.20	0.92	2.51	95.11		nd		0.00	0.00

*Sulphide sulphur nd-not determined

Table 2

The heavy metal content of the iron bearing raw materials/ *Conţinut de metale grele în materiile prime purtătoare de fier*

	Elements *Element*	Pyrite cinder *Cenuşa de pirită*	Mill scale *Ţunder*
1	Hg	**0.756**	**0.037**
2	Cd	35.20	0.44
3	Tl	5.20	0.04
∑(1-3)		**40.40**	**0.48**
4	As	4352.00	22.40
5	Co	284.00	56.20
6	Ni	73.00	530.50
7	Sb	161.00	18.80
8	Pb	4291.00	28.90
9	Cr	8.00	368.70
10	Cu	4382.00	1449.00
11	Mn	684.00	5315.00
12	V	42.00	87.70
∑(4÷12)		**14277.00**	**7877.20**

Table 3

Mill scale physical characteristics/*Caracteristicile fizice ale ţunderului*

Characteristic *Caracteristica*	Mill scale *Ţunder*
Volume weight (kg/m^3)	2170
Particle size distribution, %	
> 25 mm	-
25-15 mm	-
15-10 mm	2.8
10-7 mm	4.0
7-5 mm	6.2
5-3 mm	15.1
3-1 mm	26.5
< 1 mm	45.4

Table 4

The dosage of the raw mixes/ *Dozajul amestecurilor brute*

Specification/*Specificația*	Raw mix/*Amestec brut*	
	M 1	M 2
Dosage */ Dozaj (%)*		
Limestone / *Calcar*	69.35	69.36
Marl / *Marnă*	30.40	30.45
Pyrite cinder / *Cenuşă pirită*	0.25	-
Mill scale / *Ţunder*	-	0.19

In order to investigate the influence of mill scale addition on technological behavior of the raw mixture, based on chemical analyzes two raw mixtures were performed. A standard mixture (M1), from current raw materials (limestone, marl and pyrite cinder) and a mixture (M2) in which pyrite cinder was entirely substituted with mill scale. The raw mixes have lime saturation factor – LSF =0.98, alumina ratio =1.7 and silica ratio =2.2.

Proposed manufacturing dosages are presented in Table 4.

3.2. Raw mixes burnability

Burnability was evaluated by determining the content of free CaO on samples thermally treated at 1300°C, 1350°C, 1400°C, 1450°C and 1450°C after 30 minutes plateau.

The results obtained for free CaO determined at different temperatures highlight that the presence of mill scale in the raw mixture determines a better behavior at clinkerization. Thus, the values of free CaO are below 2% (maximum value technological recommended) starting with the temperature of 1400^{0}C (Figure 1).

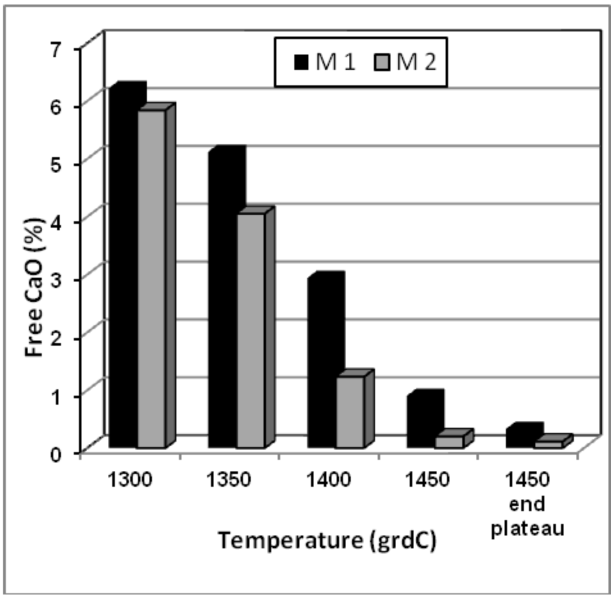


Fig. 1 - Variation of free CaO in raw mixes versus temperature / *Variația CaO liber în amestecurile brute funcție de temperatură.*

This behavior may be explained by the higher amounts of Mn and Ni and substantial amount of Cu in mill scale compared with pyrite cinder that exert a more significant mineralizing effect in the raw mix M2 [25,26].

Obtained theoretical values for the burning indicators are presented in Table 5.

The calculated values of the burnability indicators are within allowable range and are well corelated with the values practically obtained at free CaO determination, confirming a good burnability of the achieved raw mixes.

Table 5

Burnability indicators / *Indicatori de apreciere ai aptitudinii la clincherizare*

Indicator/*Indicator*	Allowable range / *Interval admisibil*	Mixtures / *Amestecuri* (%)	
		M 1	M 2
Burnability index BI / *Indicele aptitudinii la ardere BI*	2.6 – 4.2	3.26	3.06
Refractory factor RF/*Indice de refractaritate* RF	1.3 – 3.0	2.45	2.31
Burnability factor BF / *Factorul de aptitudine la ardere BF*	100 – 120	112.59	112.57
Minimum burning temperature (ºC) / *Temperatura minimă de ardere (ºC)*	-	1421	1408

In industrial practice it has been found that the ability to form clinker is well evidenced by this indicators. If the burnability index BI < 2.6 – easier to burn mixtures and if BI > 4.2 – harder to burn mixtures. For the refractory index (IR) and burnability factor (BF) if the values are in the allowable range it is considered that the raw meal has a normal burnability. Higher values for minimum burning temperature indicate a harder to burn mix.

3.3. Theoretical heat consumption at clinker formation

The calculation formula elaborated by Onoda [19] was used for estimated the theoretical heat consumption necessary for clincher formation.

The values of heat theoretic consumption was 437.95 kcal/kg in case of references raw mix (M 1) respectively 439.49 kcal/kg in case of the mixture M 2. The insignificantly difference between the two values reveal that the addition of mill scale in the raw meal does not influence considerable the theoretical heat consumption.

3.4. Chemical and mineralogical characteristics of the clinker

Chemical characteristics of the clinkers obtained through raw mixes burning in the laboratory condition and the potential mineralogical composition after Bogue relations are given in Table 6.

Table 6

The chemical composition of the clinkers
Analiza chimică a clincherelor

Characteristics *Caracteristica*	Clinker M 1	Clinker M 2
CaO, %	66.55	68.45
SiO_2, %	21.28	21.54
Al_2O_3, %	5.71	6.30
Fe_2O_3, %	3.67	3.71
MgO, %	1.34	1.69
Na_2O, %	0.66	0.65
K_2O, %	1.24	1.24
Free CaO, CaO liber %	0.25	0.19
Insoluble residue/*Reziduu insolubil, %*	0.15	0.16
C_3S, %	65.5	63.1
C_2S, %	12.9	15.5
C_3A, %	8.9	9.4
C_4AF, %	11.2	11.2

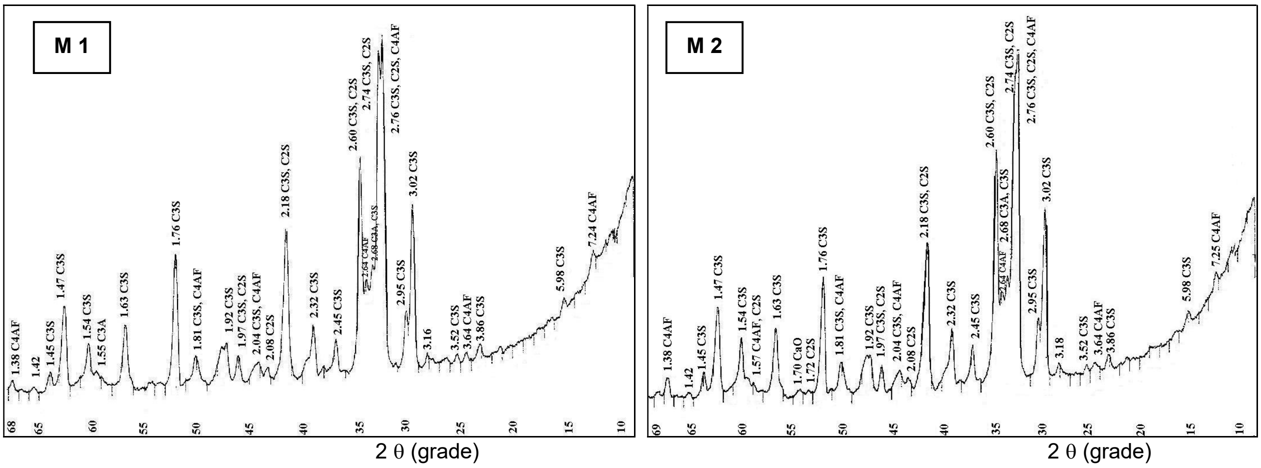
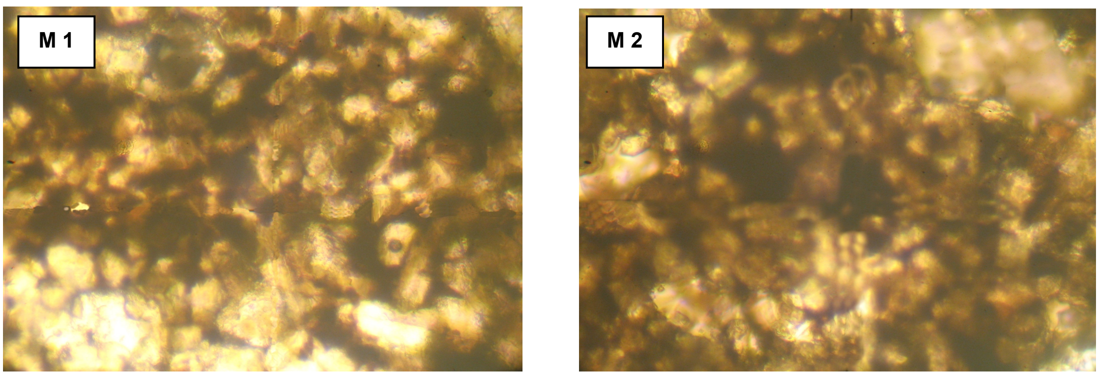


Fig. 2 - X-ray diffraction patterns of the clinkers/ *Spectrul difractometric al clincherelor.*



N II, M 300 X
Fig. 3 – Optical micrography of clinkers / *Micrografia clincherelor.*

Table 7

Mineralogical characteristics of clinkers determined by optical microscopy
Caracteristicile mineralogice ale clincherelor determinate prin microscopie optică

Caracteristica / *Characteristics*	Clinker /*Clincher M 1*		Clinker /*Clincher M 2*	
	Proportion *Proporţie*, %	Crystals size *Dimensiune cristale*, μm	Proportion *Proporţie, %*	Crystals size *Dimensiune cristale*, μm
C_3S	~ 65	5-40	~65	5-35
C_2S	~ 15	5-20	~15	5-15
Interstitial phase/ *Faza interstiţială*	~ 20	-	~20	-

Table 8

Physical- mechanical characteristics of cements / *Caracteristicile fizico-mecanice ale cimenturilor*

Physical - mechanical characteristics/ *Caracteristici fizico-mecanice*		Cement symbol/ *Simbol ciment* M 1	M 2	Conditions imposed by/ *Condiţii impuse de* SR EN 197-1
Water for standard consistency, % *Apa de consistenţă standard*		24.0	24.5	-
Setting time *Timp de priză*	Beginning / *Început, min*	130	140	≥ 45
	End / *Sfârşit, hours-min*	3-45	4-00	-
Soundness / *Stabilitate, mm*		1.0	1.0	≤ 10
Compressive strength/ *Rezistenţa mecanică la compresiune, MPa*	2 days / *zile*	22.4	21.8	≥ 20
	7 days / *zile*	42.2	40.9	
	28 days / *zile*	56.3	55.6	≥ 52.5
Strength class / *Clasa de rezistenţă*		**52.5N**	**52.5N**	**52.5N**

The mineralogical composition did not seem to be affected by the mill scale used as correction additions in the raw mix.

Mineralogical composition of the clinkers is also indicated by the X-ray diffraction pattern, presented in Figure 2.

The X-ray diffraction patterns obtained for samples M 1 and M 2 (Fig 2) indicate that the clinkers have similar qualitative phase composition. The major crystalline phases of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) are all present in the laboratory clinkers. A splitting of alite reflection at 51.7° 2θ in doublet can be faintly observed, this barely observed feature lead to the assertion that monoclinic polymorph of alite formed in clinkers, as in industrial clinkers. [27,28]

Obtained results by examination through optical microscopy of the clinker samples are presented in table 7 and the clinker micrographs are shown in the Figure 3.

From textural point of view the clinkers have a high porosity. Worthy to note is the presence of a few cracks in the clinkers mass formed during the rapid cooling of clinker. C_3S occurs as prismatic crystals which are intensely colored and with small inclusions of C_2S and fine ferrite and aluminate crystals. Alite is present mostly in monoclinic variety. Rounded crystals of belite are observed in nests with curved boundaries and very little interstitial material that suggests its formation in an environment of siliceous component.

3.5. Cement characteristics

The main physical and mechanical characteristics of the CEM I type cements obtained by grinding of clinkers together with 5% gypsum up to a finesses of 3500 cm^2/g are presented in Table 8.

Physical-mechanical characteristics of both cements are in accordance with the requirements imposed by Romanian and European norm SR EN 197-1 [20]. All values of the characteristics of the M2 cement are very close to those of M1 cement, having a good setting time and soundness. Also, the mechanical strengths developed at 2 and 28 days by the cement M 2 being in the same class, 52.5N, with that of the reference cement M 1.

4. Conclusions

The results obtained in the present investigation promote findings of interest in the development of clinkers, with mill scale recovery. The following conclusion can be draw:

- use of mill scale in the raw mixture leads to an improvement of clinker burnability;
- from textural and qualitative phase composition view point, a similarity between the clinker obtained by using current raw materials and the clinker in witch pyrite cinder was entirely substituted with mill scale was found;
- the compressive strength values assessed after 28 days allow the inclusion of both cements in the strength class 52.5N;
- it is possible to use this type of waste as Fe_2O_3's correction addition in Portland cement clinker manufacturing.

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