EFECTELE TIPULUI DE COMBUSTIBIL UTILIZAT LA ARDEREA CLINCHERULUI ASUPRA CARACTERISTICILOR ACESTUIA
EFFECTS OF FUEL TYPE USED FOR CLINKER BURNING ON THEIR CHARACTERISTICS

CARMEN (GHEORGHE) OPROIU, GEORGETA VOICU*
University POLITEHNICA of Bucharest, Str. G. Polizu nr. 1, 011061, Bucharest, Romania

The use of alternative fuels in the manufacturing of cement can influence the thermo-chemical processes in the kiln as well as the quality of the obtained clinker. Also, the use of alternative fuels has impact both from economic and environmental point of views.

In the present study are assessed the composition and microstructure of clinkers manufactured with conventional fuel i.e. coal-coke mixture, and alternative fuels - solid residual (SRF). The substitution rate of conventional combustible was 30%.

No significant differences were identify, in terms of composition (oxide and mineralogical) and microstructure for clinkers obtained using alternative (SRF) and conventional (coal-coke mixture) fuels.

Utilizarea combustibililor alternativi poate influența procesele termo-chimice care au loc în instalația de ardere pentru obținerea clincherului cât şi calitatea acestuia. Acestea au un impact atât din punct de vedere economic cât şi de mediu.

În prezentul studiu s-au determinat caracteristicile compoziționale şi microstructurale ale clincherelor obținute cu combustibil tradițional – amestec cărbune-cocs, şi alternativ- reziduuri solide (SRF). Substituirea combustibilului tradițional cu cel alternativ a fost de 30%.

Nu au fost identificate diferențe privind compoziția chimică (oxidică şi mineralogică) şi de microstructură pentru clincherele obținute utilizând combustibil alternativ (SRF) şi convențional (amestec cărbune-cocs).

Keywords: *solid residual fuels (SRF), clinker quality,composition and microstructure, Riedveld method, scanning electron microscopy*

1. Introduction

Potentially waste materials (e.g. oil, tar) or pollutant recycled materials (e.g. plastic, tyres, textiles) can be used in the processing of cement and cement-based materials. Substitution of fossil fuels in process of clinker production by waste materials (mentioned in the literature as 14% to 90%) [1] which bring in a system the similar thermal energy is called co-processing or co-incineration. Different types of substitution fuels, called alternative fuels can be used: high caloric wastes (e.g. tyres, waste oils, and plastics), dried sewage sludge, and solid residual fuels (SRF) – a mixture of plastics, wood, paper, cartons etc.

The use of alternative fuels can have an important influence on the thermo-chemical processes which occurs in the kiln as well as on the quality of the obtained clinker [1-10]. These fuels can have also impact both from economic and environmental point of views.

In the present study are assessed the composition and microstructure of clinkers manufactured with conventional fuel i.e. coal-coke mixture, and alternative fuels - solid residual (SRF). The replacement of conventional fuel was 30%.

2. Experimental

The conventional fuel was coal-coke mixture and the alternative fuel was solid residual (SRF). The replacement level of conventional fuel was 30% and the burning conditions were the same for the both clinkers.

The chemical and mineralogical compositions were assessed by X-ray diffraction (XRD) coupled with Rietveld method and X-ray fluorescence (XRF). The X-ray diffraction analyses were performed using two diffractometers with CuKα radiation: Shimadzu XRD 6000 with λ= 1.5406 Å and PANalytical CubiX with λ= 1.5418 Å. The range 2 theta was 5 to 65 degree.

X ray fluorescence spectrometry (Axios) was used for the assessment of oxide composition of clinker and heavy elements (Epsilon 5).

The microstructure characteristics - porosimetry and morphological of phases, were assessed with mercury intrusion porosimetry and scanning electron-microscopy (SEM). The mercury intrusion porosimetry was performed using a 140/240 Pascal porosimeter. SEM analyses were performed on clinkers coated with Ag, using a HITACHI S2600N microscope.

* Autor corespondent/*Corresponding author*,
E-mail: georgeta.voicu@upb.ro

3. Results and discussion

Figure 1 shows the diffraction patterns for the both clinkers i.e. A, obtained by burning with conventional fuel, and B obtained with SRF. On the XRD patterns are present the peaks specific for tricalcium silicate (C_3S, JCPDS 42-0551), dicalcium silicate (C_2S, JCPDS 24-0034), brownmillerite ($C_2(A,F)$, JCPDS 30-0226) and tricalcium aluminate (C_3A, JCPDS 33-0251). No significant changes are noticed from the point of view of the crystallinity of mineralogical phases, assessed by this method for the two studied clinkers.

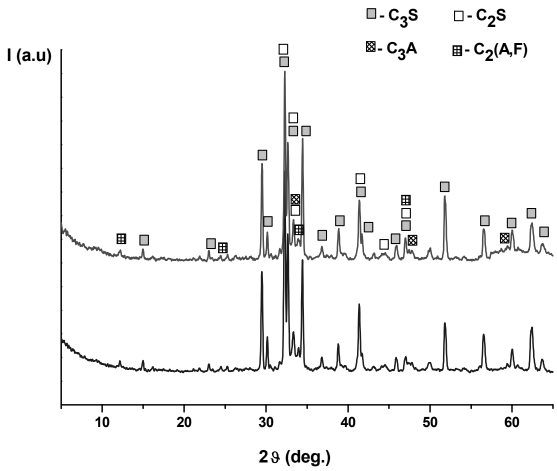

Fig. 1 - X-ray patterns for clinkers: A- burnt with conventional fuel and B- burnt with SRF / *Difractogramele clincherelor: A- ars cu combustibil tradițional şi B- ars cu combustibil alternativ de tip SRF*.

Oxide compositions of clinkers assessed by XRF are presented in Table 1. One can observe that the replacement of conventional fuel with 30% SRF do not induce important differences in their oxide composition.

Table 1

Oxide composition of clinkers A (with conventional fuel) and B (with SRF)
Compoziția oxidică a clincherelor: A- ars cu combustibil tradițional şi B- ars cu combustibil alternativ de tip SRF.

Clinker code / Oxide (%)	A	B
CaO	66.00	66.44
SiO_2	21.26	21.30
Al_2O_3	5.03	4.99
Fe_2O_3	3.01	3.13
MgO	1.24	1.25
SO_3	1.08	0.88
Na_2O	0.58	0.54
K_2O	0.77	0.65
Cl	0.002	0.004
Lime saturation factor (LSF)	97.88	98.32
Silica ratio	2.65	2.62
Aluminium ratio	1.67	1.59

The quantitative mineralogical composition, determined using Rietveld refinement method, is presented in Table 2. It can be observed that the content of free lime in clinker B is below 1% and also a slightly higher value of C_3S as compared with reference (A clinker). These results corroborated with the smaller amount of C_2S confirm a higher rate of the chemical processes that occurs during the thermal treatment and especially of the calcium disilicate conversion in C_3S.

This is expected to have a positive influence on clinkers quality because is well known that calcium silicates (C_3S and C_2S) are the main contributors to the characteristics of the cements prepared from the clinkers – especially the mechanical properties [2-4].

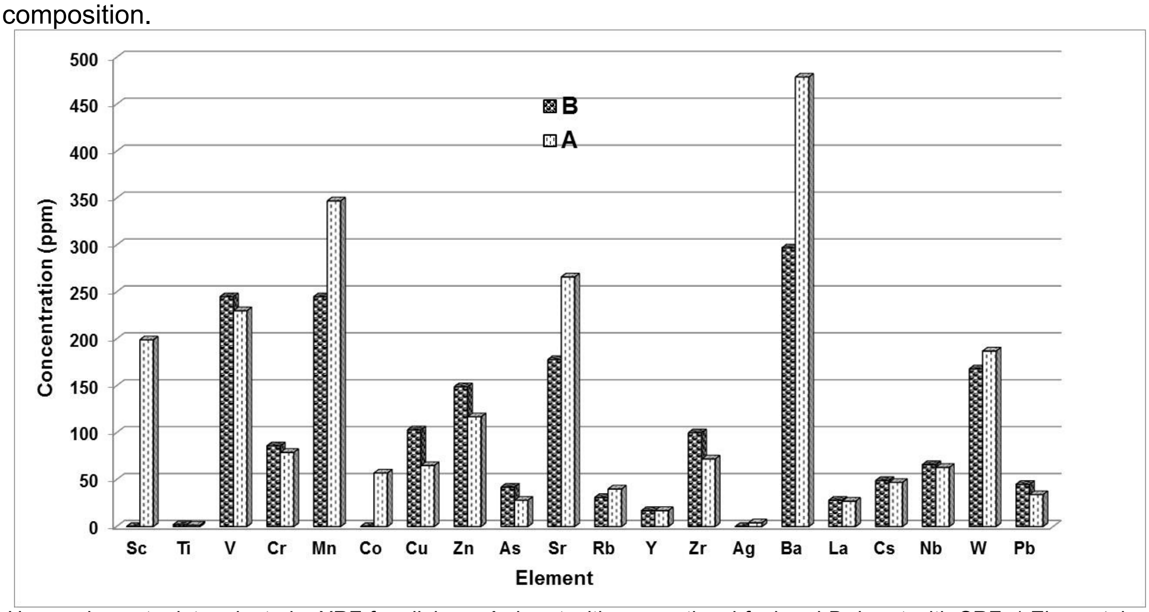

Fig. 2 - Heavy elements determinate by XRF for clinkers: A- burnt with conventional fuel and B- burnt with SRF. / *Elementele grele din clinchere determinate prin XRF: A- ars cu combustibil tradițional şi B- ars cu combustibil alternativ de tip SRF.*

Table 2

Quantitative determinations of the mineralogical composition of clinkers using Rietveld refinement

Determinări cantitative ale compozitiei mineralogice ale clincherelor obținute pe baza fitării Rietveld.

Clinker code / Phase (%)		A	B
CaO_{free}		1.07	0.87
C_3S		64.01	66.93
C_2S		17.19	14.4
C_3A	cubic	5.14	2.92
	orthorombic	2.71	4.47
	total	7.85	7.39
Arcanite (K_2SO_4)		0.52	0.61

From the point of view of heavy elements determinate by XRF for both clinkers – fig. 2, one can note that these are similar with the values indicated in literature data [11].

The clinker's porosity is an important property because influences its grindability; it is well known that during the cement manufacture process the clinker is grinded together with gypsum (compulsory) and other additions (optional). The values of clinkers porosity assessed by mercury intrusion method are presented in Figure 3 and Table 3. No significant differences were identified in terms of porosity for the studied clinkers.

Table 3

The porosity data for clinkers

Datele de porozimetrie pentru clinchere.

Clinker code	A	B
Total cumulative volume (mm^3/g)	85.425	112.69
Total specific surface area (m^2/g)	0.296	0.22
Average pore radius (micron)	13.2939	13.945
Total porosity (%)	23.1977	23.723

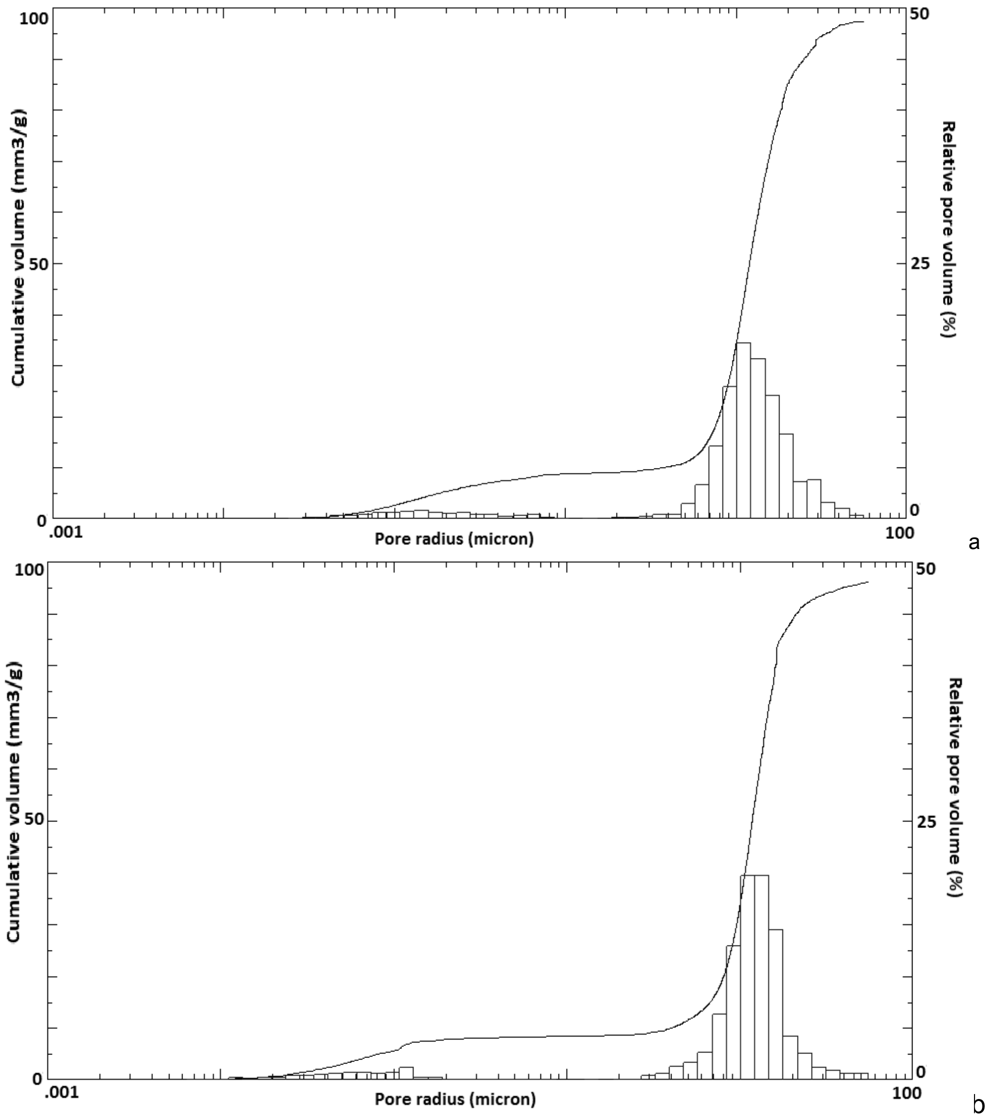

Fig.3 – Mercury intrusion porosimetry for clinkers: a- clinker A (burnt with conventional fuel) and b- clinker B (burnt with SRF). *Porozimetria cu mercur pentru: a- clincherul A (ars cu combustibil traditional) şi b- clincherul B (ars cu combustibil alternativ de tip SRF).*

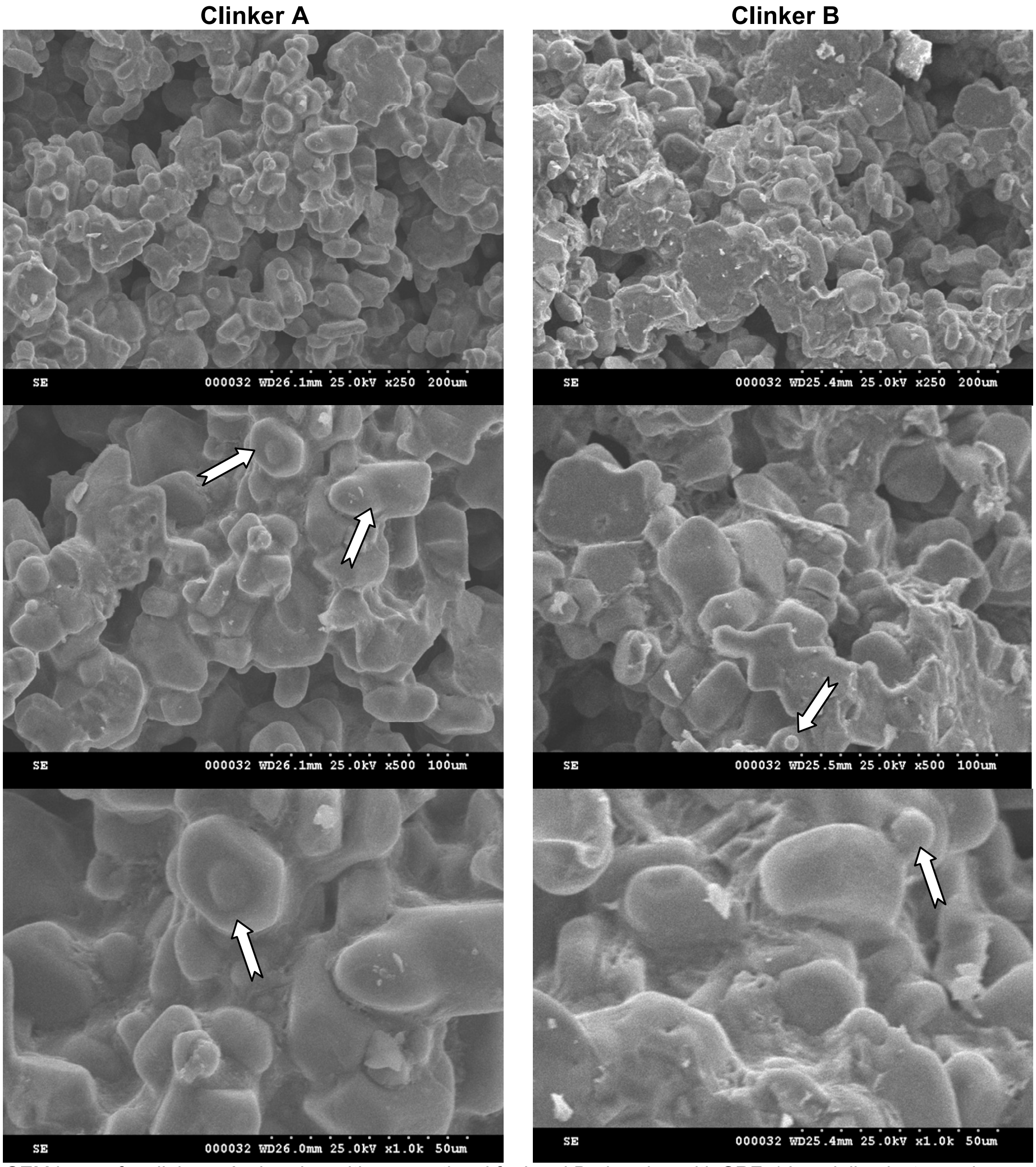

Fig. 4 - SEM image for clinkers: A - burning with conventional fuel and B - burning with SRF. / *Imaginile electron-microscopice ale clincherelor: A- ars cu combustibil tradițional şi B- ars cu combustibil alternativ de tip SRF.*

SEM images of both clinkers (A and B) are presented in Figure 4. One can identify the prismatic alite crystals and round belite crystals [12-14].

Also, there are some areas where belite crystals are present on the alite crystals surface or as inclusions in the alite crystals (see arrows). Alite crystals are locked in the vitreous interstitial phase, which smoothness their edges.

One can also notice, between the alite crystals, the ferrite crystal box works structure specific for ferite aluminate phase [12].

4. Conclusion

No significant differences were identify, in terms of composition (oxide and mineralogical) and microstructure of clinkers obtained using conventional (coal-coke mixture) and alternative (SRF) fuels - substitution rate of conventional fuel of 30%.

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REFERENCES

1. F. Pacheco-Torgal, S. Jalali and A. Fucic - Toxicity of Building Materials, Ed. Woodhead Publishing Limited- L. Tiruta-Barna, R. Barna, Cap. 14 - Potential hazards from waste based/recycled building materials, 2012, 391.
2. M. Georgescu, G. Niculae, Impact of the alternative fuels use on the composition and on the structural characteristics on the clinkers, Romanian Journal of Materials, 2010, **40** (2), 102.

3. M. Georgescu, G. Voicu, C. Stoica, Clinkers and cements obtained by using alternative fuels, Romanian Journal of Materials, 2009, **39** (2), 108.
4. D. Năstac, M. Hupa, M. Muntean, Influence of using meat and bone meal as an alternative fuel on formation and properties of Portland clinker, Proceedings of the 12th International Congress of Cement Chemistry, Montreal, Canada, 2008.
5. M.A. Trezza, A.N. Scian, Burning Wastes as an Industrial Resource: Their Effect on Portland Cement Clinker, Cement and Concrete Research 2000, **30** (1), 137.
6. A. Rahman, M.G. Rasul, M.M.K. Khan, S. Sharma, Impact of alternative fuels on the cement manufacturing plant performance: an overview, Procedia Engineering 2013, **56**, 393.
7. M. Paul, Quantification of Portland cement clinker phases by means of Rietveld analysis when using secondary fuels, Cement International 2004, **2** (5), 105.
8. R. Klaska, S. Baetzner, H. Möller, M. Paul and T. Roppelt, Effects of secondary fuels on clinker mineralogy, Cement International 2003, **1** (4), 89.
9. I. Smith, Co-utilisation of coal and other fuels în cement kilns, IEA Clean Coal Centre August 2003, 28.
10. S. Puntke and M. Schneider, Effects of phosphate on clinker mineralogy and cement properties, Cement International 2008, **6** (5), 81.
11. M. Achternbosch, K.-R. Bräutigam, N. Hartlieb, C. Kupsch, U. Richers, P. Stemmermann, Heavy metals in cement and concrete resulting from the co-incineration of wastes in cement kilns with regard to the legitimacy of waste utilization, Forschungszentrum Karlsruhe GmbH, Karlsruhe, 2003.
12. Campbell DH. Microscopical examination and interpretation of Portland cement and clinker, 2nd ed., Portland Cement Association; 1999.
13. A. Bădănoiu, J. Paceagiu, G..Voicu, Evaluation of some mineral additions effect on the burnability of raw mix in cement production, Scientific Bulletin of University POLITEHNICA of Bucharest, Series B 2009, **71** (3), 23.
14. A. Bădănoiu, J. Paceagiu, G..Voicu, Hydration and hardening processes of Portland cements obtained from clinkers mineralized with fluoride and oxides, Journal of Thermal Analysis and Calorimetry, 2011, **103** (3), 879.

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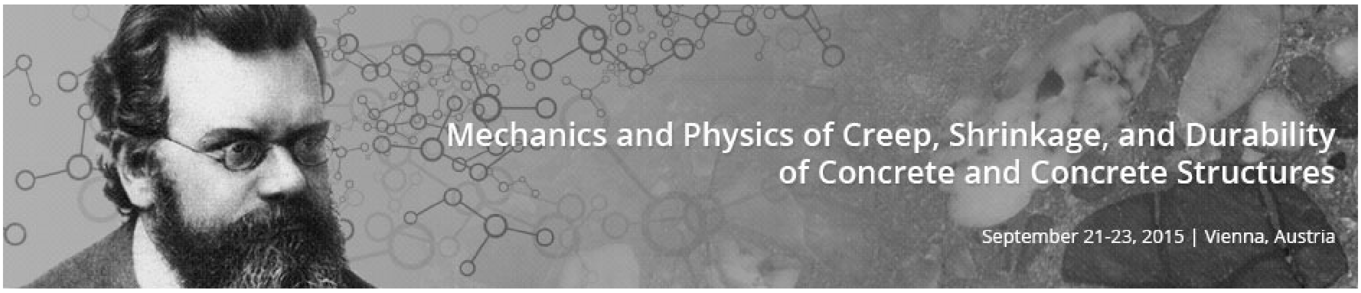
MANIFESTĂRI ŞTIINȚIFICE / SCIENTIFIC EVENTS



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