INFLUENŢA STERILULUI MINIER ŞI A NĂMOLULUI DE PETROL ASUPRA FABRICĂRII CLINCHERULUI DE CIMENT PORTLAND
THE INFLUENCE OF MINE TAILINGS AND OILY SLUDGE ON THE PORTLAND CEMENT CLINKER MANUFACTURE

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Alternative materials such as industrial wastes and by-products can be easily and economically utilised as raw material in Portland cement clinker manufacture. These materials are generated in abundance as a result of growing worldwide industrialisation. Two types of wastes from mining industry were used as secondary raw material in a concentration ranging from 1.4 to 3.5%. CEM I cements were obtained from these clinkers and compressive strength was determined. Different amounts varying between 3 and 7% of sludge generated in the effluent treatment plants of oil fields were added to a base raw mixture and the effect on the clinkering process was studied. The chemical and mineralogical compositions of the wastes and raw meals were determined. The raw mixes burnability containing different concentrations of wastes in various stages of burning in a laboratory furnace to form a Portland cement clinker was investigated. An improved burnability was noticed without affecting the clinker quality.

Materialele alternative, cum ar fi deşeurile şi subprodusele industriale pot fi cu uşurinţă şi economic utilizate ca materie primă în fabricarea clincherului de ciment Portland. Aceste materiale sunt generate din abundenţă, ca urmare a creşterii industrializării la nivel mondial. Două tipuri de deşeuri provenite din industria minieră au fost utilizate ca materie primă secundară într-o concentraţie care a variat între 1,4 şi 3,5%. Din aceste clinchere au fost obţinute cimenturi CEM I pentru care s-a determinat rezistenţa la compresiune. Diferite cantităţi de nămol generat în staţiile de tratare a efluenţilor de la câmpurile petroliere care au variat între 3 şi 7% au fost adăugate la un amestec de bază de materii prime, fiind analizat efectul asupra procesului de clincherizare. Au fost determinate compoziţiile chimice şi mineralogice ale deşeurilor şi amestecurilor de materii prime. A fost investigată aptitudinea la ardere a amestecurilor de materii prime care conţin concentraţii diferite de deşeuri, în diverse etape de ardere într-un cuptor de laborator. S-a observat o aptitudine la ardere îmbunătăţită, fără a afecta calitatea clincherului.

Keywords: *alternative raw materials, Portland cement clinker, tailing waste, effluent treatment plants sludge*

1. Introduction

The overall priority for cement makers is the safe manufacture of high quality cement. The Romanian cement industry is committed to achieving this objective in a sustainable way: environmentally, socially and economically [1-3]. To achieve greater sustainability, it is essential that all available resources be used efficiently and effectively. The cement industry considers wastes, with some exceptions, as alternative resources awaiting an appropriate use and is actively pursuing beneficial use within its manufacturing processes [4]. The Romanian Government has committed itself to the EU Landfill Directive 1999/31/EC that aim to reduce disposal of wastes to landfill and to recover energy and materials from used tyres, packaging wastes, solvents and many other waste streams. The cement industry is, therefore, playing a vital role in helping to achieve the environmental objectives by using appropriate wastes as alternative fuels and raw materials in the manufacture of cement [5,6].

The main indicators of cement quality are the requirements for mechanical, physical and chemical properties and are standardised in European/national product specifications [7]. These requirements must be met regardless of either the type of fuel used or the nature of the raw materials. These properties are measured and monitored continually, under independent third party inspection, in order to ensure that cement conforms to its specification and can be legally placed on the market. The use of wastes has no effect on these major properties because any potential effects will have been accounted for by making compensatory adjustments to the chemical composition of the raw material fed to the kiln.

Portland cement is made from mixtures of mainly natural materials, chiefly limestone and

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clay/marl. These raw materials can be partially replaced by wastes and by-products from other industries in order to ‘adjust’ the overall chemical composition. The alternative raw materials used are mainly inorganic, carefully sourced and subject to specifications to which suppliers must comply. The ability to consume large quantities of waste materials in cement manufacture arise from a long residence time and high temperatures in clinker kilns that ensures the complete breakdown of the raw materials into their component oxides and recombination of the oxides into the clinker minerals. Alternative raw materials currently in use are: fly ash [8-10], foundry sand [11], blastfurnace slag [12,13], and steel slag [14,15], mill scale and dusts from steel production, lime sludge from drinking water and sewage treatment [5,16], paper residuals [17], ashes from incineration processes [18], residues from reprocessing salt slag [19] or pyrite cinders [20]. Work is also underway to introduce wastes rich in silica, and lime from, for example, glass industry [21].

From the perspective of resource recovery and recycling, the use of mine tailings and sludge from effluent treatment plants as raw materials for cement production is of interest, but it was scant investigated [22,23]. Large volumes of various waste tailings and dredged materials are generated yearly around the world by the mining and dredging industry. According to the last available Eurostat data, it was estimated that during 2012, 801 million tones of wastes originated mainly from mining industry in European countries. This kind of waste is typically fine-grained material with low permeability and rate of consolidation [24]. These properties contribute to stability problems in their disposal and containment, which potentially lead to possible environmental contamination.

Prior to being refined to petroleum products, crude oil is temporarily stored in tanks, where it has the tendency to separate into heavier and lighter petroleum hydrocarbons. The heavier fraction often settles along with solid particles and water being known as oily sludge. It has been estimated that one ton of oily sludge waste is generated for every 500 tons of crude oil processed [25] and is expected that the total oily sludge production amount is still increasing as a result of the ascending demand on refined petroleum products worldwide. These sludges have to be treated and made harmless before disposal. Oily sludge is mixed with various solvents in the effluent treatment plant in order to break down complex molecules present in the sludge into their basic constituents (water, crude oil and particulate). After separation the waste residues is further treated by centrifugation and components are separated on the basis of their densities. This latter waste is defined as sludge generated in the effluent treatment plants (ETPs) of oil fields.

The aim of the present research work was to investigate the possibility of adding mine tailings from settling ponds in the raw meal for the production of Portland cement clinker. Also, the effect of the addition of different amounts of sludge generated in the ETPs of oil fields in the clinkering process of Portland cement was studied.

2. Materials and methods

2.1. Raw materials characterization

The experiments performed in the present study used a raw mixture sample to which were added different amounts of mine tailings and sludge generated in the ETPs of oil fields, respectively. The basic raw mixture consisted of limestone, clay and pyrite cinder and its particle size distribution is presented in Figure 1. The distribution of the particles size is characterized by a median diameter d(0.5) of 9.685 µm, surface weighted mean D[3,2] of 4.165 µm, volume weighted mean D[4,3] of 34.695 µm and the width of the distribution is 10.643. The particle size distribution of the raw mixture was determined using a Malvern Matersizer 2000E laser granulometer.

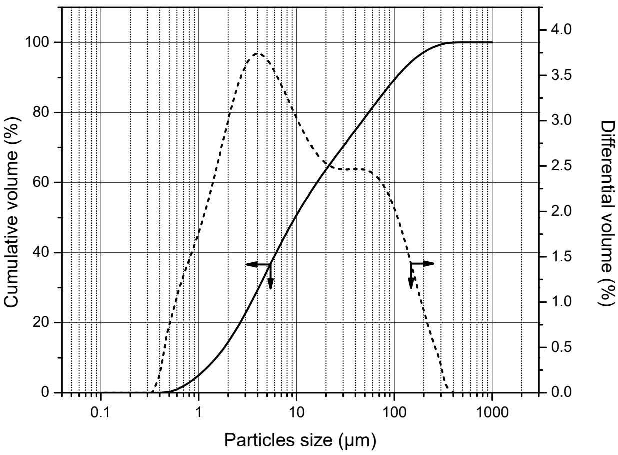

Fig. 1- Particle size distribution of the basic raw mixture / *Distribuția dimensiunii particulelor pentru amestecul de bază de materii prime.*

Three samples of raw meals with mine tailings taken from two settling ponds, named D and Z, were prepared. Mine tailings were added to the raw meal in a concentration ranging from 1.4 to 3.5%. These samples were named MT-D1, MT-D2 and MT-Z. Mine tailings was used as replacement for siliceous components in the raw feed because of its rich content in silica, as can be observed in Table 1. Additionally, the effect on clinker burning of sludge generated in the ETPs of oil fields has been investigated for two reasons, as a substitute for ferrous components in the raw mixture and as potential use as alternative fuel due to its high net calorific value (see Table 1). Sludge sample was dried at 105°C in an oven for 24 h until it reached a constant weight. Sludge generated in the ETPs of oil fields was mixed with raw meal in a concentration of 3, 5 and 7%. These samples were named S-ETP-3, S-ETP-5 and S-ETP-7. The chemical analysis of ETP sludge's ash is also presented in Table 1. The ash content of the ETP sludge was 11.7%.

Table 1

Chemical analysis of the alternative materials used for Portland cement clinker manufacture / *Analiza chimică a materialelor alternative utilizate la obținerea clincherului de ciment Portland*

Oxides/ *Oxizi*	Content of the alternative materials (% wt.) / *Conținut de materiale alternative (% masa)*		
	D mine tailings/ *Steril minier D*	Z mine tailings/ *Steril minier Z*	ETP-T waste*/ *Deseu ETP-T*
SiO_2	83.70	77.79	23.04
Al_2O_3	1.72	5.28	8.32
Fe_2O_3	0.58	8.65	20.46
CaO	7.30	0.81	15.61
MgO	0.20	0.39	1.09
SO_3	0.05	1.19	14.31
Na_2O	0.10	0.13	1.34
K_2O	0.15	1.52	1.16
LOI	6.02	4.13	11.03
H_S (kJ/kg)	n.d.	n.d.	21462
H_I (kJ/kg)	n.d.	n.d.	19933

* oxide composition of the obtained ash / *compoziția oxidică a cenușii obținute*
n.d. – not determined / *nedeterminat*
LOI – loss on ignition / *pierderea la calcinare*
H_S – higher heating value (gross calorific value) / *puterea calorifică superioară*
H_I – lower heating value (net calorific value) / *puterea calorifică inferioară*

Sludge generated in the ETP of oil fields contains both crystalline (calcite and quartz) and amorphous phase or very poorly crystalline phases, according to X-ray diffraction pattern presented in Figure 2. Amorphous phase was assigned based on two broad hints: the feeble hump in the data between 2θ = 22 – 48° and raised background level. The high background level is also due to iron content of the sample which in turn causes fluorescence by CuKα radiation of the X-ray diffractometer tube. A silicon zero background plate was useful to differentiate between the two contributions due to amorphous content and iron fluorescence on background [26].

The substitution rate of dredge waste and ETP of oil fields for traditional raw materials was determined by taking into account the alternative materials composition, the Bogue calculation, the lime saturation factor (LSF), the silica ratio (SR) and the alumina ratio (AR). In the formulation of clinker's raw mixture it was considered previous study [27], that pointed out that to minimize free lime content, the best solution is to obtain a rich content in calcium aluminate (C_3A) and calcium aluminate ferrite (C_4AF). The raw mixes were obtained by grinding the raw materials according to the formulations presented in Table 2. The raw mixes were ground up to a fineness value of 10% residue on the 90μm sieve and, finally, the resulted mixes underwent characterisation in terms of chemical composition and clinker burnability.

The sintering process applied was identical for all compositions. The raw mixes were shaped in small spheres, with a diameter of maximum 30 mm, and dried at 110°C. Then, they were placed inside a furnace and the temperature increased up to 1450°C and it was maintained constant for sintering process that took 30 min. At the end of the sintering process, the samples were removed from the furnace and left to cool in air. The quantities of clinker produced in the laboratory are limited to the size of the furnace available.

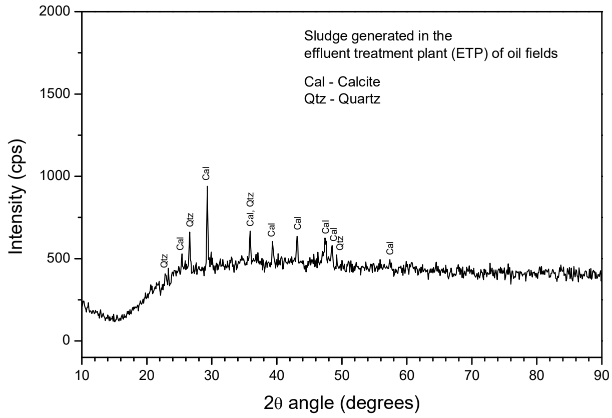

Fig. 2 - Mineralogical phases of ETP sludge assessed by XRD
Fazele mineralogice ale nămolului ETP evaluate prin XRD.

2.2. Methods

The burnability of raw mixes was assessed by free lime determination. Thus, one clinker nodule was removed from the furnace at various stages of burning regime: 1300°C, temperature specific to solid state reaction zone that slightly overlaps with clinkering zone, 1350, 1400, 1430 and 1450°C. For the last mentioned temperature it was considered the beginning and the end of the flat region of the temperature regime curve.

Table 2

Modular composition of the raw mixes / *Compoziția modulara a amestecului de materii prime*

Modular composition / *Compoziția modulară*	MT-D1	MT-D2	MT-Z	S-ETP-3	S-ETP-5	S-ETP-7
LSF	0.97	0.97	0.97	1.00	0.96	0.93
SR	2.50	2.20	2.50	1.91	1.82	1.74
AR	1.50	1.50	1.97	1.44	1.30	1.19

The chemical composition of clinkers was obtained by wet chemistry using the standardised method described in [28]. The mineralogy of the clinkers was studied by means of X-ray diffraction (XRD) using a CuKα radiation, a scanning interval 2θ between 8 and 75°, with a step of 0.05°. The clinker phases microstructure was also observed through optical microscopy on etched polished sections using a Zeiss Axio Imager petrographic microscope.

Clinkers MT-D1, MT-D2 and MT-Z were ground and mixed with 5 %wt. gypsum in order to obtain CEM I cement. The cements were ground to a specific surface area of about 3500 cm^2/g. The obtained cements underwent determinations of physical and mechanical properties.

3. Results and discussion

3.1. Raw mixes burnability and clinkers composition

The burnability of the raw mixes obtained with mine tailings and ETP waste was assessed by determining the content of free lime at various temperatures. The results are presented in Table 3. The obtained values had rather a comparative significance between the various kinds of obtained laboratory clinkers. The measures can strictly be justified only for the laboratory kiln and set of operating conditions previously presented.

In case of MT series of samples, burnability decreases with increasing LSF and SR. Increase in LSF implies more CaO that has to react, and increase in SR implies less liquid at a given temperature. The AR is relevant for clinkering temperatures below 1400°C, because it then greatly affects the quantity of liquid and the temperature at which substantial formation of liquid begins, but at 1400°C and above its effect is smaller. The temperature at which melting begins is also affected by the contents of minor components, such as MgO, Al_2O_3 and Fe_2O_3 [29]. A higher burnability it was observed for clinker MT-Z, obtained from raw mix with dredge waste. After the temperature at which liquid phase appear the process of lime combination takes place more rapidly than in the case of MT-D1 and MT-D2 raw mixes. This is probably attributed to the higher Fe_2O_3 (a fluxing agent) content of Z mine tailings comparing with D mine tailings which decrease the viscosity of the melt. According to Bucchi [30], a lower viscosity of the melt allows a higher mobility of different ionic structures in the melt. The reduced viscosity strongly promotes alite formation by accelerating dissolution of lime and belite and diffusion through the liquid. But, nevertheless, the authors are aware that effects on melt viscosity cannot be explained only on the base of iron oxide content, other minor components creating a much more complicated and sometimes confusing picture. In case of S-ETP series of samples, an increase of lime combinability with increasing sludge amount in clinker is observed. The high content of ETP-T waste in Fe_2O_3 and Al_2O_3 prove to be beneficial for raw mixture burnability. It is well known that both oxides promote the formation of alite by increasing the quantity of melt at a given temperature.

Burnability is affected by the particle size of the raw mix, and especially by the contents of coarse particles. During calcination, large particles of calcite and of siliceous materials are converted into aggregates of lime crystals and clusters of belite crystals respectively. The size distributions of these large particles determine the time required during the last stages of clinkering, when the free lime content reach its final value. According to particle size distribution presented in Figure 1, the 45 and 125 μm particles represents less than 2.5% and 1.5% of the total volume of all particles, respectively. For assessing burnability at 1400°C, the proportions of calcite particles larger than 125 μm, and of quartz particles larger than 45 μm, are particularly important [31].

According to X-ray diffraction patterns presented in Figure 3, above 1300°C, the liquid phase appears and this promotes the reaction between belite and free lime to form alite. The major crystalline phases C_3S, C_2S, C_3A and C_4AF are all present in the clinker. The obtained clinkers had high contents in tricalcium silicate. Table 4 comprehensively presents the chemical

Table 3

The free lime content at various temperatures / *Conținutul de CaO liber la diverse temperaturi*

Temperature (°C) / *Temperatura (°C)*	Free lime (% wt.) / *CaO liber (% masa)*					
	MT-D1	MT-D2	MT-Z	S-ETP-3	S-ETP-5	S-ETP-7
1300	12.30	9.52	9.77	11.64	10.92	10.43
1350	5.42	6.62	5.32	5.54	5.48	5.33
1400	2.99	2.91	2.78	2.91	1.88	1.78
1430	1.92	2.21	1.85	2.36	0.96	0.45
1450, beginning of flat temperature curve / *1450, început palier temperatură*	1.00	1.41	0.86	1.53	0.64	0.13
1450, end of flat temperature curve / *1450, sfârșit palier temperatură*	0.95	0.67	0.61	1.40	0.52	0.11

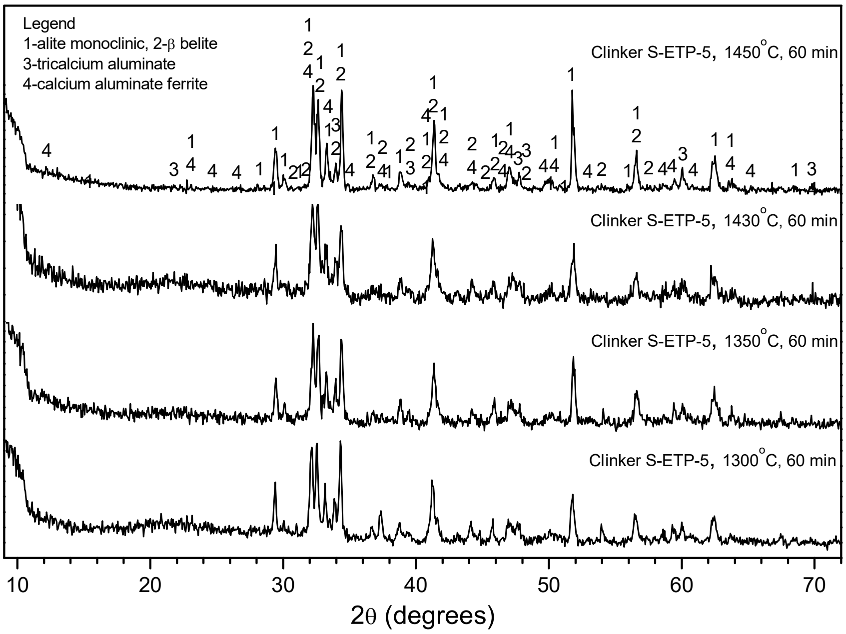

Fig. 3 - XRD patterns of S-ETP-5 series of clinkers at different temperatures / *Difractogramele RX ale seriei de clinchere S-ETP-5 la diferite temperaturi.*

Table 4

The chemical and potential mineral composition of the obtained clinkers
Compoziția chimică și compoziția mineralogică potențială a clincherelor obținute

Oxides	Clinker MT-D1	Clinker MT-D2	Clinker MT-Z	Clinker S-ETP-3	Clinker S-ETP-5	Clinker S-ETP-7
SiO_2	20.84	21.47	21.92	20.93	20.48	20.23
Al_2O_3	5.58	5.11	5.47	6.54	6.34	6.27
Fe_2O_3	3.97	3.76	3.59	3.88	3.77	3.78
CaO	67.77	68.22	68.13	65.78	66.56	67.42
MgO	0.90	0.90	0.40	1.00	0.80	1.00
SO_3	0.10	0.02	0.00	0.95	0.83	0.52
Insoluble residue	0.13	0.22	0.16	0.10	0.09	0.14
LOI	0.31	0.15	0.22	0.46	0.45	0.24
Clinker potential mineral composition / *Compoziția mineralogică potențială a clincherului*						
C_3S	68.0	70.4	66.0	59.5	64.5	67.9
C_2S	8.8	8.8	13.4	14.7	9.8	6.5
C_3A	8.1	7.2	8.4	10.8	10.4	10.2
C_4AF	12.1	11.4	10.9	11.8	11.5	11.5

characteristics on the basis of which the potential mineral composition was calculated. These results indicate that the control of compositional parameters produced the target crystalline phases in our experimental conditions.

The aim of revealing the effect of using the dredge waste and ETPs sludge in the raw mix preparation led to the conclusion that there were no significant changes in the mineral composition of the clinker. The clinkers are mostly alitic and their content in C_3S is close to the proposed one.

3.2. Clinkers' microstructure

The clinkers' microstructures observed in the silicates reflect a complex genetic history. As can be seen in Figure 4, for S-ETP series of clinkers it was noticed euhedral to subhedral, zoned, blue alite, round belite with typical multidirectional lamellae, and a well-differentiated matrix of aluminate (C_3A) and ferrite (C_4AF). Alite crystals, for the most part, nucleate and grew within the melt. The matrix is an intimate, finely microcrystalline intergrowth of aluminate and

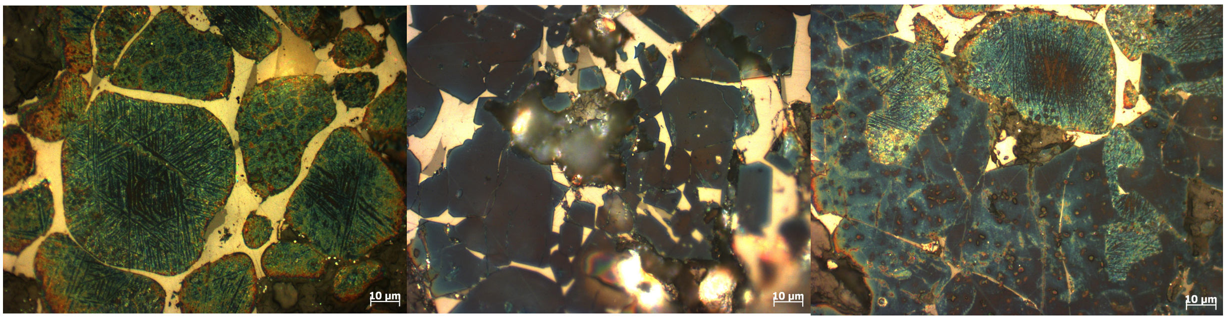

Fig. 1 - Optical microscopy photographs on etched polished sections of clinkers S-ETP-3, S-ETP-5 and S-ETP-7 / *Imagini de microscopie optică pe secțiunile șlefuite ale clincherelor S-ETP-3, S-ETP-5 și S-ETP-7 atacate selectiv*

Table 5

The physical and mechanical properties of the CEM I cements obtained with MT clinkers
Proprietățile fizice și mecanice ale cimenturilor CEM I obținute cu clincherele MT

Sample / *Proba*		Cement / *Ciment*		
		MT-D1	MT-D2	MT-Z
Blaine specific surface area (cm^2/g) / *Suprafața specifică Blaine (cm^2/g)*		3510	3530	3500
Water of normal consistency (%) / *Apa de consistență normală (%)*		24.2	24.0	24.2
Initial setting time (min) / *Timp inițial de priză (min)*		135	110	190
Final setting time (min) / *Timp final de priză (min)*		180	150	240
Expansion, Le Chatelier (mm) / *Expansiune, ace Le Chatelier (mm)*		0.5	1.0	0.0
Compressive strength (N/mm^2) / *Rezistența la compresiune (N/mm^2)*	2 days / *2 zile*	18.6	17.0	15.3
	7 days / *7 zile*	37.9	26.9	34.0
	28 days / *28 zile*	56.6	57.9	60.6
Resistance class / *Clasa de rezistență*		42.5 N	42.5 N	42.5 N

ferrite which formed during the very early cooling stage above 1300°C. Clinkers S-ETP had a LSF rather lower, and during the burning regime there was a tendency to overburn the clinker, giving rise to low levels of free lime but large alite crystals. As can be seen in Figure 4, for clinker S-ETP-7 alite crystals grew within the melt and exhibit inclusions of belite. This shows that alite formed during the heating stage as well as in the cooling stage of the burning process.

3.3. Physical and mechanical properties

Clinkers MT-D1, MT-D2 and MT-Z were ground with highly 5% wt. pure gypsum and cements CEM I were obtained. The obtained cements underwent determinations of physical and mechanical properties, the results being presented in Table 5.

The obtained values showed that the use of mine tailings in the raw mix only slightly affected the water content for standard consistency among laboratory prepared cement samples. As comparison values, for instance, for an interlaboratory CEM I 52.5N that has a Blaine specific surface of 3380 cm^2/g, the water of normal consistency statistically determined after elimination of erroneous values was 25.6% [32]. The expansion measured, according to the Le Chatelier process, was well below the maximum accepted value of 10 mm according to specifications and conformity criteria for common cements presented in [7]. The low expansion values arise from the reduced content of free calcium and magnesium oxides in these cements. Setting time was influenced by the type of mine tailing. As can be seen from the data presented in Table 5 the highest values were obtained for Z mine tailings which has the lowest alite content among MT cements. Many researchers have concluded that setting is controlled by the hydration of alite [33]. Initial set is reported to correlate with the end of the induction period, although this time is not always well defined. Final set is said to occur about mid-way through the acceleration period. The mortars of the samples tested for compressive strengths after 2, 7 and 28 days of curing showed the highest value for Z mine tailings. As the value of the early age strength at 2 days is between 10 and 20 N/mm^2, even though the standard strength at 28 days meets the requirements for a 52.5 N cement, the assigned strength class is 42.5 N [7].

4. Conclusions

From the present study the following conclusions can be drawn:

- Mine tailings from settling ponds can be used as corrective materials to the raw mix in cement manufacture.
- Mine tailings and sludge generated in the ETPs of oil fields affect positively the burnability of raw mix, due to influences on melt properties
- Clinkers of normal modular composition and a higher silica ratio than the normal clinkers (without additives) can be obtained with mine tailings as alternative raw material.
- The use of mine tailings in the raw mix only slightly affected the water content for standard consistency among laboratory prepared CEM I cement samples.
- The expansion measured was well below the maximum accepted value of 10 mm and the setting time had the highest value for cement with the lowest alite content, obtained with Z mine tailings.
- The compressive strengths of cements obtained with mine tailings classifies them in a higher resistance class, i.e. 42.5 N.

Acknowledgements
This work was undertaken in the framework of the program "Partnership in priority areas-PN II", developed with the support of MEN-UEFISCDI, project no. 223, code PN-II-PT-PCCA-2013-4-1808 and project no. 31-011.

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