DE GRUYTER OPEN

DOI: 10.2478/sspjce-2015-0020

Effect of Selected Alternative Fuels and Raw Materials on the Cement Clinker Quality

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Abstract

The article deals with the study of the effects of alternative fuels and raw materials on the cement clinker quality. The clinker quality was expressed by the content of two principal minerals alite C_3S and belite C_2S. The additions of alternative fuels ashes and raw materials, in principle, always increased the belite content and conversely reduced the amount of alite. The alternative fuels with high ash content were used such as the meat-bone meal, sewage sludge from sewage treatment plants and paper sludge and the used alternative raw materials were metallurgical slags - granulated blastfurnace slag, air cooled blastfurnace slag and demetallized steel slag, fluidized bed combustion fly ash and waste glass. Meat-bone meal, sewage sludge from sewage treatment plants and paper sludge were evaluated as moderately suitable alternative fuels which can be added in the amounts of 2.8 wt. % addition of meat-bone meals ash, 3.64 wt. % addition of sewage sludge ash and 3.8 wt. % addition of paper sludge ash to the cement raw mixture. Demetallised steel slag is suitable for production of special sulphate resistant cement clinker for CEM I –SR cement with addition up to 5 wt. %. Granulated blastfurnace slag is a suitable alternative raw material with addition 4 wt. %. Air cooled blastfurnace slag is a suitable alternative raw material with addition 4.2 wt. %. Waste glass is not very appropriate alternative raw material with addition only 1.16 wt. %. Fluidized bed combustion fly ash appears not to be equally appropriate alternative raw material for cement clinker burning with less potential utilization in the cement industry and with addition 3.41 wt. %, which forms undesired anhydrite $CaSO_4$ in the cement clinker.

Key words: alternative fuels, alternative raw materials, clinker quality

1 Introduction

The growth of alternative fuels and raw materials utilization in the cement industry has been enormous in the recent decade [1-3]. The reason is accompanied with economic as well as environmental aspects. Environmental aspects consist in the effort of saving depletable fossil fuels and nature raw materials, decreasing CO_2 emissions and waste deposits, saving landfill space and supporting at environmental pollution reduction. The worldwide annual production of cement is responsible for about 5% of the total CO_2 emission [4]. However, the use of bio-fuels or alternative fuels with some biomass content can decrease CO_2 emissions due to the fact, that the biomass is CO_2 neutral, since it is utilized for the growth of next biomass [5]. Economic aspects are connected with creating added value by substituting expensive fossil fuels with the cheaper or cost-less secondary fuels and the cost-less or negative cost wastes. The same effect is also reached by reducing exploitation of quarry raw materials by replacing with secondary raw materials or wastes.

The cement production enables an energy and materials recovery and waste disposal in a great extent. Unbeatable and unique advantages of the burning of alternative fuels and wastes in the cement rotary kilns are as follows: high combustion temperatures about 2000 °C in the main flame and 1400-1500 °C of the burned clinker and guaranteed oxidizing atmosphere during firing, sufficiently long retention time of fired substrates in the areas with high temperatures, non-waste incineration of organic substrates without producing ash, since forming ashes are immediately built in the creating clinker structure being fired, utilization of the heat and material content of organic substrates and saving fossil fuels, formation of non-toxic combustion gases CO_2, NO_X, H_2O, O_2 without a possibility of backward formation of harmful halogenated organic compounds containing dioxins and furans, acidic gases such as HCl, HF and SO_X are highly captured by alkaline preheated and precalcinated raw mixture with high content of free lime CaO [6]. The alternative fuels commonly used in the cement industry are as follows [2, 3]: solid - used tyres, rubber wastes, plastics, textile, thermal fraction of domestic, municipal and industrial wastes, sewage sludge from wastewater plants, animal meals (rendering plant by-product), as well as solid biofuels such as contaminated wood, by-products from wood treatment, paper sludge, paper, cardboard etc.; liquid - waste oils, spent solvents, waste paints, distillation residues, animal fat etc.; gaseous – pyrolysis gas, landfill gas, gas from anaerobic digestion of sewage sludge from wastewater plants etc. From the given kinds of alternative fuels, only solid alternative fuels (SAF) contain ash in such amount, that they can affect the mineralogical composition of clinker and so the cement quality. The standard EN 15357 [7] defines SAF as solid recovered fuel prepared from non-hazardous waste to be utilized for energy recovery in incineration or coincineration plants and meeting the classification and specification requirements laid down in EN 15359 [8]. The standard EN 15359 [8] introduces the new classification system for SAF, which classifies them into 5 qualitative classes according to 3 basic classification characteristic values such as net calorific value, chlorine and mercury content. The standard EN ISO 16559 [9] defines solid biofuels including waste demolition wood arising from demolition of buildings or civil engineering installations. The new classification system for solid biofuels is introduced by standard EN ISO 17225-1 [10].

The alternative raw materials (ARM) usually utilized in the cement industry are as follows [2]: metallurgical slags, wastes from metal industry, siliceous and calcareous fly ashes, circulating fluidized bed combustion fly and bottom ashes, spent foundry sand, construction and demolition debris, carbide lime, contaminated soil, red and brown mud, roasted pyrite cinder, gypsum from gas desulphurization, chemical gypsum etc.

The limitations for using SAF and ARM are fulfilling the emission limits during their burning, their maximal contents of pollutants such as heavy metals, halogenated organic compounds (PAHs, PCBs etc.) and the presence of problematic chlorine, sulphur, sodium and potassium compounds. The restrictions are given by laws, regulations and directives [11, 12]. Any kind of SAF and ARM has an impact on the burning conditions during firing of the clinker and the quality of clinker, its microstructure and product properties [13, 14].

The SAF and ARM affect the raw mixture composition, its reactivity and burnability. Each element possesses own influence on clinker composition and properties [13, 14]. Sodium Na, commonly occurring element in SAF, with higher amounts in meat-bone meal (MBM), has effect on setting behaviour, causes the formation of orthorhombic C_3A instead of cubic C_3A or alkali sulphate according to the degree of sulphatisation of clinker. The amount of reactive orthorhombic C_3A decreases with increasing sulphatisation in clinker. Potassium K, also commonly occurring element in alternative fuels, has very similar effect on the cement quality as sodium. Generally, alkali Na and K promote higher early strength and lower long term strength. High levels of alkali are not required because they can cause alkali-silica reaction in the concretes containing aggregates with alkali sensitive constituents.

Sulphur S is volatile, forms alkali sulphates which influence setting behaviour. Sulphur in alite causes the growth of enlarged crystals. Chlorine Cl is volatile, forms alkali chlorides, which are formed sooner than alkali sulphates and so influences the degree of clinker sulphatisation. After evaporating chlorine and sulphur, they form cycles in the kiln system atmosphere, raise the undesired coating layers, build-ups and rings. They support an agglomeration of large clinker nodules. High levels of chlorides are not required, because they promote the concrete and reinforcing steel chloride-induced corrosion. Fluorine F mainly in gypsum from neutralization of acidic solutions used for polishing lead crystal glass, lowers melting point, increases C_3S formation, up to 0.5 % increases early strength, then has retarding effect. Aluminium Al mainly from food aluminum foils, wrappers and packets increases the amount of interstitial mass, promotes higher clinker reactivity, increases strength development. Iron Fe at local reducing burning conditions is subject to the reduction of Fe^{3+} to Fe^{2+}. Fe^{2+} in contrast to Fe^{3+} is compatible with alite structure and can be incorporated into alite. The subsequent oxidation of Fe^{2+} in alite structure under oxidizing conditions causes decomposition of alite to belite and free lime and so the loss of strength and a possible effect on soundness. This effect causes less C_4AF formation and more C_3A and affects the setting behaviour, because the settnig is faster. Phosphate P mainly from MBM or sewage sludge stabilizes C_2S and so causes the decrease of C_3S amount, retards the strength development, which has adverse effect on the cement quality. Higher amounts of phosphate lead to the formation of solid solution C_2S-C_3P with the crystal structure of β–C_2S, α'-C_2S and α-C_2S, moreover the last modification has no hydraulic properties. The content of P_2O_5 is the main limitation factor for the increasing of MBM cofiring [15, 16]. The belite C_2S content increasing connected with alite C_3S decreasing every time means the decrease of early strengths and hydration heat development, but the increase in chemical durability. American standard ASTM C 150 [17] designates the Portland cement with mineralogical composition containing up to 35 wt. % of C_2S and up to 45 wt. % of C_3S as the Type IV: portland cement having a low heat of hydration, while Portland cement for general use, which is known also as ordinary Type I, can contain up to 30 wt. % of C_2S and up to 65 wt. % of C_3S [17].

The aim of the article is the evaluation of effect of SAF and ARM on the clinker phase composition resulting from belite content increasing and so to interpret the suitability and amount of SAF and ARM for clinker production without any quality loss.

2 Materials and methods

A common industrial cement raw mixture (RM) with chemical composition given in Table 1 and was used for the laboratory burnings. In order to prevent the influence of random large particles, the original RM was additionally ground to pass the aperture size of the sieve of 0.2 mm, with maximum 1 % residue and thoroughly homogenized. Then the effect of RM granulometry on the clinker phases forming rate was studied at constant temperature of 1430 °C and on two RMs with different granulometries. The reference was industrial raw mixture with maximum 1 % residue on a 90 µm sieve and the laboratory prepared one with granulometry of maximum 1 % residue on 200 µm sieve. The effect of selected SAF and ARM on the clinker phases formation was performed by means of the calcined SAF ashes and by dried ARMs. MBM ash was prepared under laboratory conditions by MBM thermal treatment at 650 °C for 1 hour in an oxidizing atmosphere in laboratory kiln and the ash of sewage sludge from waste water plants and ash of paper sludge were calcinated at 800 °C for 1 hour. Their chemical composition is given in Table 1 as well, and the mineralogical composition is described down. The calcined ashes as well as dried raw materials were spread in agate mortar to very fine powder (with fineness more than 400 m^2/kg). After the fine ashes and dried ARMs adding into RM up to maximal 5 wt. % (at MBM ash maximal 8 wt. %), the experimental mixtures were mixed and then thoroughly homogenized, which ensured the homogeneity of the experimental mixtures without presence of local differences in the concentration.

Table 1: The chemical composition of the used common industrial cement raw mixture (RM), the ashes of alternative fuels such as (ash of meat-bone meal (AMBM), ash of sewage sludge from waste water plants (ASS), ash of paper sludge (APS)) and the alternative materials (granulated blastfurnace slag (GBS), air cooled blast-furnace slag (ABS), demetallized steel slag (DSS), fluidized bed combustion fly ash (FCFA), waste glass (WG)).

wt. %	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	Na_2O	K_2O	SO_3	Cl^-	L.o.I.
RM	14.73	3.14	1.92	43.03	1.04	0.06	0.19	0.69	0.36	0.02	34.80
AMBM	1.56	0.15	0.69	45.89	1.52	34.40	3.39	3.09	0.86	2.86	5.52
ASS	42.06	17.08	5.62	20.30	1.62	5.64	0.28	0.42	4.79	0.72	0.89
APS	24.51	14.13	0.79	57.09	3.45	0.22	0.08	0.63	0.78	0.26	0.02
GBS	42.17	6.87	0.32	41.92	10.39	0.05	0.17	0.60	1.84	0.02	0.95
ABS	40.57	8.12	2.81	41.73	8.44	0.14	0.19	0.72	2.39	0.01	0.09
DSS	12.81	1.64	29.78	52.30	2.54	0.48	0.07	0.04	0.28	0.01	6.02
FCFA	40.99	21.24	7.80	25.86	3.22	0.76	0.31	0.99	9.07	0.02	3.11
WG	75.58	0.33	0.21	6.73	4.23	0.03	14.66	0.61	0.46	0.04	0.01

Cylindrical pellets were pressed out from the mixtures to the constant volume weight 2.6 $g.cm^{-3}$ and the size 10 mm diameter x 20 mm height. The pellets were burnt in a specially modified laboratory kiln with a sliding manipulator containing platinum holder for samples. 4 cylindrical pellets were pressed out from each mixture. Manipulator of the specially modified kiln moved the pellet in to the centre of the kiln firing zone having been preheated to 1430 °C, and after the lapse of burning time, the clinker was equally removed from the kiln and freely cooled in the kiln. The burning duration of pellets from the basic raw mixtures without addition of SAF or ARM was 15 and 30 minutes for granulometry of maximum 1 % residue on a 90 µm sieve and 20 and 40 minutes for granulometry of maximum 1 % residue on 200 μm sieve at standard firing conditions. At the other cases, the burning time was chosen according to the phase composition development. The burnt clinkers were analyzed by XRD analysis connected with Rietveld computation of quantitative analysis of clinker minerals [18]. The clinker quality was expressed mainly by the content of two principal clinker minerals alite C_3S and belite C_2S. The limit for belite C_2S content in the experimental clinker has been chosen on 20 wt. %. Small amount of the samples did not allow testing the mechanical and physical characteristics of the cements.

Mineralogical composition of SAF and ARM is as follows: AMBM – hydroxylapatite $Ca_5(PO_4)_3OH$, calcite $CaCO_3$, whitlockite $Ca_3(PO_4)_2$ (C_3P), sodium calcium phosphate β-$NaCaPO_4$, quartz SiO_2, sylvite KCl; ASS – quartz SiO_2, dolomite $CaMg(CO_3)_2$, calcium phosphate $Ca_3(PO_4)_2$ (C_3P), maghemite Fe_2O_3, hematite Fe_2O_3, calcium iron oxide C_2F, anhydrite $CaSO_4$, gehlenite C_2AS, brownmillerite C_4AF; APS – calcite $CaCO_3$, quartz SiO_2, free lime CaO, portlandite $Ca(OH)_2$, anhydrite $CaSO_4$; GBS – glassy matrix with very small amount of melilite - solid solution of gehlenite C_2AS and akermanite C_2MS_2 crystals identified; ABS – melilite - solid solution of gehlenite C_2AS and akermanite C_2MS_2, brownmillerite C_4AF, quartz SiO_2; DSS – wüstite FeO, brownmillerite C_4AF, free lime CaO, portlandite $Ca(OH)_2$, belite β-C_2S, quartz SiO_2; FCFA – quartz SiO_2, anhydrite $CaSO_4$, free lime CaO, anorthite CAS_2, hematite Fe_2O_3, magnetite Fe_3O_4; WG – fully glassy phase.

3 Results and discussion

3.1 The firing of common industrial cement raw mixture

The maximal possible alite C_3S content reachable by the firing of the used common industrial cement raw mixture (RM) has been tested on the 2 basic raw mixtures - with granulometry of maximum 1 % residue on 200 μm fired 20 minutes (RM1) and 40 minutes (RM2) and with granulometry of maximum 1 % residue on a 90 μm sieve fired 15 minutes (RM3) and 30 minutes (RM4). The additional grinding below 90 μm has been applied to eliminate the coarse particles influence on the rate of clinker phase development as much as possible and to increase the reactivity of raw mixtures.

Table 2: The phase composition of clinkers prepared from industrial cement raw mixtures.

wt. %	C_3S	C_2S	C_3A c	C_3A o	C_4AF	C_{free}	M	Q	K_2SO_4	CH
RM 1	64.89	17.83	4.33	0.00	10.47	1.57	0.36	0.37	0.00	0.18
RM 2	72.17	14.10	2.44	0.00	9.43	0.69	0.53	0.36	0.00	0.29
RM 3	73.02	10.27	5.69	0.51	9.53	0.40	0.30	0.19	0.00	0.11
RM 4	77.55	7.94	3.69	0.00	9.67	0.09	0.55	0.52	0.00	0.00

The granulometry of the raw mixture influences the reactivity i.e. reaching maximal possible alite C_3S content in the cement clinker during time unit in a great extent. The maximal alite C_3S content 77.55 wt. % with minimal reached belite content C_2S 7.94 wt. % has been achieved at raw mixture RM4. However, the granulometry of the common industrial cement raw mixtures is in the range about 1 % residue on 200 μm and so the alite C_3S content 72.17 wt. % with belite content C_2S 14.10 wt. % is decisive for practical industrial applications. The limiting belite C_2S content in the fired experimental clinkers chosen on the level 20 wt. % has not been exceeded in all cases. Therefore all alternative fuel ashes and raw materials rich in SiO_2 content together with low CaO content increase the belite C_2S content in the clinker. The content of interstitial matter consisting of C_3A and C_4AF, which forms liquid phase - melt during firing, has been increased by increasing reactivity but it has been decreased with prolonged firing time. The content of cubic C_3A in comparison with content of orthorhombic one has been strongly predominant due to very low alkalis in the used common industrial cement raw mixture. At low amount of alkalis available, cubic C_3A is formed having moderate reactivity. On the other hand, at high amount of alkalis available, orthorhombic C_3A is formed having enhanced reactivity. Amount of reactive orthorhombic C_3A also decreases with increasing degree of sulphatisation in the clinker, i.e. with rising sulphur content in the added alternative fuel ashes and raw materials. The degree of sulphatisation of alkalis in the clinker can be seen on the base of arcanite K_2SO_4 content, however its content is also very strongly dependant on the evaporation at high temperatures. The content of unbound quartz SiO_2 (Q) in the clinker (cement insoluble residue comprises mainly unbound quartz SiO_2) represent the part of raw mixture with the lowest reactivity consisting of large particles of quartz and hornfels, the influence of which can be diminished by additional grinding under 45 μm, where the mineralogical effect is suppressed in a great extent. The content of free lime C_{free} has been decreasing with rising reactivity of raw mixture as well as the duration of firing time and not exceeded the limiting value 2.5 wt. %, after which the clinker can be volumetrically unstable with undesired expansion. Portlandite $Ca(OH)_2$ (CH) in clinker is formed by hydration of very active free lime C_{free} with air humidity. With decreasing free lime C_{free} content, the alite C_3S content has been increased and belite C_2S content has been decreased, as well.

3.2 Addition of granulated blast-furnace slag

The experimental mixture (EM) consisting of 5 wt. % fine granulated blastfurnace slag (GBS) and 95 wt. % industrial cement raw mixture (RM) has been studied on the base of 2 basic experimental mixtures having been fired at 1430 °C - with granulometry of maximum 1 % residue on 200 μm fired 20 minutes (EM1) and 40 minutes (EM2) and with granulometry of maximum 1 % residue on a 90 μm sieve fired 15 minutes (EM3) and 30 minutes (EM4).

Table 3: The phase composition of clinkers prepared from EM containing GBS and RM.

wt. %	C_3S	C_2S	C_3A c	C_3A o	C_4AF	C_{free}	M	Q	K_2SO_4	CH
EM 1	58.02	24.93	2.28	1.15	12.30	0.22	0.68	0.13	0.00	0.28
EM 2	58.85	24.88	2.28	0.49	12.60	0.10	0.49	0.18	0.00	0.14
EM 3	60.21	22.43	3.30	0.80	12.20	0.08	0.51	0.03	0.04	0.38
EM 4	60.54	22.90	2.63	0.51	12.54	0.00	0.49	0.06	0.00	0.33

From the results in Table 3 it can be seen, that the addition of 5 wt. % GBS to the industrial cement RM has undesirably increased the belite C_2S content in the clinker over the limit 20 wt. % with appropriate alite C_3S content decrease. The highest belite C_2S content 24.93 wt. % has been achieved at experimental mixture EM 1, which decreased by 2 wt. % with increasing of reactivity and firing time, together with adequate increase in alite C_3S content. The content of cubic C_3A has been decreased with simultaneous orthorhombic C_3A content increase in comparison with the pure raw mixture. The low content of free lime C_{free} proofs the mineralized effect of fine granulated blastfurnace slag on clinker phases development. GBS is a suitable alternative raw material with recommended addition maximal 4 wt. % that does not exceed the limit 20 wt. % belite C_2S content in the clinker.

3.3 Addition of air cooled blast-furnace slag

The experimental mixture (EM) consisting of 5 wt. % fine air cooled blast-furnace slag (ABS) and 95 wt. % industrial cement raw mixture (RM) has been studied on the base of 2 basic experimental mixtures having been fired at 1430 °C - with granulometry of maximum 1 % residue on 200 µm fired 20 minutes (EM5) and 40 minutes (EM6) and with granulometry of maximum 1 % residue on a 90 µm sieve fired 15 minutes (EM7) and 30 minutes (EM8).

Table 4: The phase composition of clinkers prepared from EM containing ABS and RM.

wt. %	C_3S	C_2S	C_3A c	C_3A o	C_4AF	C_{free}	M	Q	K_2SO_4	CH
EM5	58.29	24.66	2.83	0.32	12.07	0.61	0.63	0.35	0.00	0.24
EM6	59.11	23.77	1.81	0.95	13.47	0.09	0.48	0.16	0.00	0.16
EM7	58.09	24.47	2.77	0.93	13.03	0.00	0.39	0.17	0.05	0.11
EM8	46.85	32.75	4.61	1.70	13.18	0.00	0.29	0.36	0.16	0.10

From the results in Table 4 it can be seen, that the addition of 5 wt. % fine ABS to the industrial cement RM also has undesirably increased the belite C_2S content in the clinker over the limit 20 wt. % with appropriate alite C_3S content decrease like in the case of GBS. Both slags have relatively the same chemical composition, but very different mineralogical composition due to their cooling regime. The highest belite C_2S content 32.75 wt. % has been achieved in the case of experimental mixture with granulometry of maximum 1 % residue on a 90 µm sieve fired 30 minutes (EM8), simultaneously with the lowest alite C_3S content 46.85 wt. %, which is unacceptable values. The high SiO_2 content of fully crystallized ABS, mainly in the form of quartz SiO_2, has negatively proved on the C_3S/C_2S ratio in a great extent, in contrary to the high SiO_2 content of practically fully glassy GBS, where the glassy phase had a little intensifying effect on clinker forming reactions. The great decrease of alite C_3S content in experimental mixture EM8 has been connected with the slight increase in cubic C_3A as well as orthorhombic C_3A content. Therefore ABS is not so appropriate alternative raw material than GBS, however it can be recommended the maximal addition 4.2 wt. % of ABS to the cement RM with the granulometry of 1 % residue on 200 µm being fired for 40 minutes, not to exceed the limit 20 wt. % belite C_2S content in the clinker. In this case, ABS can be stated as a suitable alternative raw material.

3.4 Addition of demetallized steel slag

The experimental mixture (EM) consisting of 5 wt. % fine demetallized steel slag (DSS) and 95 wt. % industrial cement raw mixture (RM) has been studied on the base of 2 basic experimental mixtures having been fired at 1430 °C - with granulometry of maximum 1 %

residue on 200 µm fired 20 minutes (EM9) and 40 minutes (EM10) and with granulometry of maximum 1 % residue on a 90 µm sieve fired 15 minutes (EM11) and 30 minutes (EM12).

Table 5: The phase composition of clinkers prepared from EM containing DSS and RM.

wt. %	C_3S	C_2S	C_3A c	C_3A o	C_4AF	C_{free}	M	Q	K_2SO_4	CH
EM9	74.49	5.58	0.05	0.00	18.22	0.40	0.47	0.63	0.00	0.16
EM10	70.20	9.02	0.64	0.00	19.10	0.01	0.58	0.32	0.00	0.12
EM11	74.66	5.25	0.36	0.31	18.46	0.00	0.40	0.51	0.04	0.00
EM12	68.76	8.40	1.07	0.01	21.26	0.00	0.14	0.36	0.00	0.00

The very high Fe_2O_3 amount in DSS compared to blastfurnace slags has caused the increase in C_4AF content over 18 wt. % and on the other hand the decrease of C_3A content down near to zero value. The high ratio of CaO/SiO_2 predominantly favoured formation of high amount of alite C_3S in the clinker, the content of which has decreased in a little extent by firing time on behalf of belite C_2S content, which has increased from approx. 5 wt. % up to maximal 9.02 wt. % in experimental mixture EM10 (Table 5). The low content of free lime C_{free} proofs the intensifying effect of fine DSS on clinker phases development. After adding 5 wt. % fine DSS, the interstitial matter practically consists of C_4AF phase with very low C_3A content, which predominates the utilization of DSS for a synthesis of special clinkers with low C_3A content suitable for the production of high sulphate resistant portland cements CEM I – SR.

3.5 Addition of fluidized bed combustion fly ash

The experimental mixtures (EM) consisting of 2.5 wt. % fluidized bed combustion fly ash (FCFA) and 97.5 wt. % industrial cement raw mixture (RM) marked as (EM13) and 5 wt. % fine FCFA and 95 wt. % RM marked as (EM14) with granulometry of maximum 1 % residue on 200 µm were fired at 1430 °C for 30 minutes in order not to loss excessively sulphates by evaporation. The results are given in Table 6. The firing of finer RM with granulometry of maximum 1 % residue on a 90 µm sieve with increased reactivity has not been realized due to very strong mineralizing effect of sulphates on clinkering process.

Table 6: The phase composition of clinkers prepared from EM containing FCFA and RM.

wt. %	C_3S	C_2S	C_3Ac	C_3Ao	C_4AF	C_{free}	M	Q	K_2SO_4	CH	$CaSO_4$
EM13	67.06	15.22	5.10	0.29	10.60	0.87	0.42	0.12	0.00	0.25	0.04
EM14	45.88	29.34	9.35	1.66	4.90	2.45	0.67	0.43	0.00	0.01	5.27

Very high amount of sulphates SO_3 in the form of anhydrite $CaSO_4$ in FCFA compared to the other tested materials has given the reason for an assumption of formation sulphate containing compounds such as ye'elimite (Klein's compound) phase $3CaO.3Al_2O_3.CaSO_4$ being formed by reaction of calcium aluminates with anhydrite. However no ye'elimite compound has been found on XRD pattern, only unreacted anhydrite $CaSO_4$ has been clearly identified. The 2.5 wt. % addition of FCFA to the industrial cement raw mixture has resulted in the clinker with usual phase composition. However, 5 wt. % addition of FCFA has provided the clinker with very high amount of belite C_2S 29.34 wt. % together with low alite C_3S content on the level

45.88 wt. %. The 5 wt. % addition also has changed the composition of interstitial matrix. The amount of cubic C_3A has been increased up to 9.35 wt. % value while C_4AF content has been decreased down to 4.90 wt. %. There has been an inappropriate increase in C_{free} content on the level of 2.45 wt. %, which can cause undesired expansion of volumetrically unstable clinker. The 5 wt. % addition of FCFA is fully unacceptable. Therefore, FCFA appears to be worse alternative raw material for cement clinker burning with less potential utilization in the cement industry and with maximal addition 3.41 wt. %, which forms undesired $CaSO_4$.

3.6 Addition of powdered waste glass

The experimental mixtures (EM) consisting of different amounts of fine powdered waste glass (WG) added to the industrial cement raw mixture (RM) with granulometry of maximum 1 % residue on 200 μm have been studied by firing 3 basic experimental mixtures at 1430 °C for 20 and 40 minutes: experimental mixtures consisting of 1 wt. % fine powdered WG and 99 wt. % industrial cement RM fired at 1430 °C for 20 (EM15) and 40 minutes (EM16); experimental mixtures consisting of 3 wt. % fine powdered WG and 97 wt. % industrial cement RM fired at 1430 °C for 20 (EM17) and 40 minutes (EM18); experimental mixtures consisting of 5 wt. % fine powdered WG and 95 wt. % industrial cement RM fired at 1430 °C for 20 (EM19) and 40 minutes (EM20).

Table 7: The phase composition of clinkers prepared from EM containing WG and RM.

wt. %	C_3S	C_2S	C_3A c	C_3A o	C_4AF	C_{free}	M	Q	K_2SO_4	CH
EM15	60.69	21.32	5.44	1.42	8.92	1.50	0.28	0.20	0.05	0.18
EM16	65.49	17.27	4.72	1.20	10.06	0.82	0.21	0.20	0.00	0.03
EM17	48.67	29.35	7.83	4.00	8.18	0.59	0.11	0.39	0.29	0.59
EM18	51.77	28.43	5.77	3.54	9.32	0.13	0.33	0.22	0.00	0.49
EM19	41.53	33.93	9.96	5.72	7.31	0.10	0.07	0.33	0.30	0.73
EM20	35.53	42.17	7.53	4.45	9.16	0.11	0.20	0.38	0.02	0.44

Very high amount of SiO_2 compared to low CaO content in the powdered WG predestines the use of this alternative raw material for a production of special belite clinkers with low development of strengths according and low heat of hydration in accordance with American standard ASTM C 150 [17]. Already 1 wt. % addition of fine powdered WG has increased the belite C_2S content in the clinker over limit 20 wt. %. With increasing addition of fine powdered WG, the belite C_2S content has been gradually increased at the expense of alite C_3S content decreasing. At 5 wt. % addition of fine powdered WG in experimental mixture EM20, the belite C_2S content reached twice the limiting amount 42.17 wt. % C_2S at the level of alite C_3S content 35.53 wt. %, which are not acceptable values. Very high amount of Na_2O in WG promotes increased formation of reactive orthorhombic C_3A. With the increasing of addition of fine powdered WG, the content of reactive orthorhombic C_3A has been gradually increased as well as the content of cubic C_3A, the contents of which have decreased in a little extent with burning time on account of the increase of C_4AF in a little extent as well. The low content of free lime C_{free} proofs the intensifying effect of fine powdered WG on clinker phase development. WG is the worst alternative raw material with addition only 1.16 wt. % possible.

3.7 Addition of meat-bone meal ash

The experimental mixtures (EM) consisting of 4 wt. % fine meat-bone meal ash (AMBM) i.e. containing 1.5 wt. % P_2O_5 and 96 wt. % industrial cement raw mixture (RM) marked as (EM21) and 8 wt. % meat-bone meal ash (AMBM) i.e. containing 3.0 wt. % P_2O_5 and 92 wt. % industrial cement raw mixture (RM) marked as (EM22) with granulometry of maximum 1 % residue on 200 μm were fired at 1430 °C for 40 minutes.

Table 8: The phase composition of clinkers prepared from EM containing AMBM and RM.

wt. %	C_3S	C_2S	C_3A c	C_3A o	C_4AF	C_{free}	M	Q	K_2SO_4	CH
EM21	52.61	28.94	3.30	2.56	10.22	1.20	0.21	0.10	0.05	0.81
EM22	34.59	42.06	5.22	4.96	8.03	2.98	0.15	0.00	0.13	1.88

In practice, as long as phosphate P_2O_5 contents are less than 1 wt.-% in cement clinker, no detrimental effects on product quality are found [15, 16]. However, phosphates P_2O_5 being present in AMBM has very strong retarding effect on alite C_3S formation reaching the minimal value 34.59 wt. % at simultaneous maximal belite C_2S content of 42.06 wt. % at the level of 3 wt. % P_2O_5 in experimental mixture (EM22). This extreme case with high P_2O_5 amount is connected also with high amount of free lime C_{free} 2.98 wt. % and simultaneously high content of hydrated portlandite $Ca(OH)_2$ 1.88 wt. % in the clinker, which makes the clinker volumetrically unstable with undesired expansion. Higher amount of alkalis Na_2O and K_2O in the powdered AMBM has promoted the increased formation of reactive orthorhombic C_3A. MBM can be evaluated as moderately suitable alternative fuels which can be added in the amounts of 2.8 wt. % addition of AMBM to the cement RM, which causes the increase P_2O_5 content in the clinker on the level of 1.05 wt. %.

3.8 Addition of sewage sludge ash from waste water plants

The experimental mixture (EM) consisting of 5 wt. % fine ash of sewage sludge from waste water plants (ASS) and 95 wt. % industrial cement raw mixture (RM) has been studied on the base of 2 basic experimental mixtures having been fired at 1430 °C - with granulometry of maximum 1 % residue on 200 μm fired 20 minutes (EM23) and 40 minutes (EM24) and with granulometry of maximum 1 % residue on a 90 μm sieve fired 15 minutes (EM25) and 30 minutes (EM26).

Table 9: The phase composition of clinkers prepared from EM containing ASS and RM.

wt. %	C_3S	C_2S	C_3A c	C_3A o	C_4AF	C_{free}	M	Q	K_2SO_4	CH
EM23	48.32	25.01	4.17	4.58	16.80	0.06	0.12	0.51	0.15	0.29
EM24	46.63	27.48	5.14	2.94	16.89	0.04	0.08	0.29	0.09	0.42
EM25	52.52	22.04	4.57	4.38	15.71	0.00	0.00	0.38	0.10	0.30
EM26	44.47	30.20	4.26	3.77	16.42	0.05	0.12	0.16	0.11	0.45

The additions of 5 wt. % fine ASS having high SiO_2/CaO ratio to cement raw mixture has possessed strong retarding effect on alite C_3S formation reaching the minimal value 44.47 wt.

% at simultaneous maximal belite C_2S content 30.20 wt. % (EM26). The retarding effect has been supported also by increased P_2O_5 content on the level 5.64 wt. % from the detergents from households.The amount of alite C_3S has been decrease with firing time on behalf of increasing belite C_2S content in the clinker. The high amount of Al_2O_3 has promoted the formation of orthorhombic C_3A. The amount of total interstitial matter consisting of C_3A and C_4AF has been increased on the levels more than 24 wt. %, which is the highest value from all alternative fuel ashes and alternative having been added to experimental mixtures. The high amount of interstitial matter formed a high amount of liquid phase - melt during firing, which has promoted the clinker phase forming reactions and so very low amount of free lime C_{free} and very low portlandite $Ca(OH)_2$ content in the clinker. Sewage sludge can be evaluated as moderately suitable alternative fuels which can be added in the amounts of 3.64 wt. % addition of ASS to the cement raw mixture.

3.9 Addition of paper sludge ash

The experimental mixture (EM) consisting of 5 wt. % fine ash of paper sludge (APS) and 95 wt. % industrial cement raw mixture (RM) with granulometry of maximum 1 % residue on 200 µm (EM27) and with granulometry of maximum 1 % residue on a 90 µm sieve (EM28) fired at 1430 °C for 40 minutes.

Table 10: The phase composition of clinkers prepared from EM containing APS and RM.

wt. %	C_3S	C_2S	C_3A c	C_3A o	C_4AF	C_{free}	M	Q	K_2SO_4	CH
EM27	57.24	26.63	2.67	0.37	12.38	0.00	0.15	0.32	0.00	0.24
EM28	51.92	31.38	1.99	0.80	13.14	0.00	0.40	0.20	0.00	0.17

The addition of 5 wt. % fine APS to industrial cement RM has increased the belite C_2S content in the clinker over limit 20 wt. %. With increasing reactivity of experimental mixture with additional grinding under 90 µm, the belite C_2S content has been increased on the level 31.38 wt. % at the expense of alite C_3S content decreasing to 51.92 wt. %. Higher amount of Al_2O_3 in APS has increased orthorhombic C_3A content only in small extent, however total C_3A content is not so high in comparison with the composition of clinker fired from pure RM, because a part of Al_2O_3 has been consumed on C_4AF formation. The 0.00 wt. % value of C_{free} and very low portlandite $Ca(OH)_2$ content proofs the intensifying effect of fine powdered APS on clinker phase development. Paper sludge can be evaluated as moderately suitable alternative fuels which can be added in the amounts of 3.8 wt. % addition of APS to the cement raw mixture.

4 Conclusion

All tested alternative fuels and raw materials have possessed a great effect on clinker phases development. High amount of SiO_2 increased belite C_2S content on account of alite C_3S. Increased amount of alkalis promoted reactive orthorhombic C_3A. Meat-bone meal, sewage sludge from sewage treatment plants and paper sludge were evaluated as moderately suitable alternative fuels for production of common Portland clinker. Granulated blastfurnace slag and air cooled blastfurnace slag are suitable alternative raw materials for portland clinker. Demetallised steel slag is suitable for production of special sulphate resistant cement clinker. Fluidized bed combustion fly ash and waste glass are the worse alternative raw materials of all.

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