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Waste ammunition as secondary mineralizing raw material in Portland cement production

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Abstract

This paper presents a laboratory scale simulation that aims to investigate the possibility of partially substituting ordinary cement raw mix with waste ammunition materials (WAM), originated from a shooting range in Athens, Greece, in Portland cement clinker production. One reference and twelve modified mixtures, containing 0.5%, 1.0%, 1.5% and 2.0% w/w of three blends of corresponding types of waste ammunition materials, were examined. It was concluded that the three used WAM blends, improve remarkably the burnability of the cement raw mixture, even though in a different extent, without affecting considerably the hydration rate and the cement properties. In spite of the high volatile matter in the WAM, primarily due to high levels of lead present, incorporation degree of the heavy metals present in the WAM blends in the mineralogical clinker compounds was rather high during the sintering process. Leaching tests showed that the heavy metal concentrations in the leachates were kept low.

Keywords: Waste ammunition; Cement raw mix; Clinker; Mineralizers; Volatility

1. Introduction

The environmental impact of toxic heavy metals such as Pb (lead), Cu (copper), Zn (zinc), Sb (antimony), Sn (tin), Ni (nickel), Cr (chromium), Cd (cadmium), Hg (mercury), As (arsenic) etc., has been extensively reviewed in the past. One specific source of the above metals, especially Pb and Sb, is different kinds of manufactured ammunition. Due to its special properties such as softness, high specific gravity, and low cost for production, lead is considered as a suitable material for making bullet cartridges and airgun pellets and therefore difficult to be replaced by other materials. Antimony is added in varying proportions in order to harden the bullet, depending on the characteristics needed. On the other hand, the case of the cartridge consists of different brass alloys and contains varying levels of Cu, Zn, Ni, Sn, Fe, Sb, Cd etc.

Published studies have shown the random composition of bullet alloys due to different types of produced ammunition [1–5]. Different concentrations for trace elements can be detected even for cartridges of the same type and manufacturer [6]. Taking into account that in some cases the crushed bullets or fragments settle down in the wider area of the shooting range and remain without been collected manually, they may enter and contaminate, in the long run, the soil layer. Even if to the authors' knowledge very few quantitative data are known with regard to the amounts of accumulated spent ammunition in shooting ranges, according to a recent published work [7], in Finland, a country that not only produces ammunition for recreational shooting but also has one of the biggest number of functional shooting ranges in Europe, a mean value of more than 7000 kg of shot material/year/shooting range and approximately the same mean value for bullet cases is speculated. These magnitudes vary, of course, from country to country and the

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above numbers might probably be found increased in countries with higher population of active shooters involved not only with Olympic shooting events but also with other sports that incorporate shooting (p.e. biathlon).

In most of the countries that produce ammunition, the major portion goes to military purposes, and although very little are known, the used material in some cases is collected and recycled. On the other hand, ammunition that is manufactured to be used for other purposes, such as clay and target shooting, generally is not recycled after its usage, due to the extended heterogeneity (accumulation of different types of spent ammunition), variable chemical composition and the relatively high cost for manual collection (in comparison to the cost for manufacture) that the waste ammunition material (WAM) exhibits. Hence spent ammunition (both crushed bullets, fragments and cartridge cases) is more likely to be left in the shooting range for a future disposal in dumps or sanitary landfills. Therefore from the above remarks it is conceivable that WAM has to be considered as a potential environmental hazardous waste material and precautions should be taken considering its disposal in the environment. Despite of the extended literature on remediation technologies for industrial wastes prior to disposal in landfills or directly on site [8], little published data are available concerning the fate of WAM. One option, apart from recycling, could be the use of the waste ammunition as a secondary raw material for the production of Portland cement clinker.

The use of alternative raw materials in cement industry that can be used as mineralizers or fluxes, in order to improve the burnability of the raw mix, and the effect of minor components on the formation of the clinker has been broadly discussed and reviewed adequately [9–18]. Previous relative work from the author has led to the conclusion that certain foreign elements, despite their low concentration, exert a remarkable effect on the sintering process by improving the reactivity of the raw mix and affecting the crystal structure and texture of clinker minerals, and the hydration reactions [17–25]. It must be noted, however, that when several elements are jointly present in the mixture, the reactivity is not additively changed and any secondary material that is expected to have a positive effect on the reactivity must be individually investigated.

This work aims to investigate the capability to substitute cement raw mix with WAM in cement clinker production, as a mineralizing additive. The addition of WAM in the cement raw meal will introduce varying concentrations of minor foreign elements, such as Pb, Cu, Zn, Sn, Sb etc., hence the possible use of that waste material in industrial scale will cause environmental concerns with regard to heavy metal emissions, especially for Pb, Cu and Zn. In previous published works it was well established that lead compounds are quite volatile under sintering conditions [18,26–30] but small amounts can still be retained in clinker. Pb oxide acts as a retarder during hydration [13]. On the other hand Cu in the form of CuO acts as mineralizer by decreasing the melt temperature by at least 50 °C, even for 0.5% w/w addition in the raw meal, and favors the combination of free lime even at 1100 °C [31]. Similarly, the addition of ZnO improves the burning behavior of the raw mix and accelerates the clinker formation. ZnO is also known to act as a mineralizer, leading to higher activity and promoting the solid reactions as well as the formation of alite by increasing the amount of liquid phase [32–34]. To avoid the aforementioned problems, a varying content of three blends prepared by properly treated WAM types, not exceeding 2.0% w/w, was introduced in a conventional cement raw meal. The reactivity of the modified mixtures, the sintering reactions and the structure of selected sintered products were investigated. In addition, the effect of the added waste material on the hydration rate and some of the mechanical–physical properties of the produced cements were examined. Additionally, leaching tests were carried out in order to assess any potential environmental risk from a possible application of a cement originated from such modified clinkers.

2. Experimental

2.1. Materials

Three different types of WAM were used in this study: Type 1 (T1) was manually collected from ten individual butt stoppers of 10 m paper target devices, and corresponds to 4.5 mm (0.177″) caliber crushed airgun pellets and fragments. Type 2 (T2) was manually collected from ten individual butt stoppers of 25 and 50 m paper target devices, and corresponds to 5.6 mm (0.22″) and 7.62–9.65 mm (0.30–0.38″) caliber crushed bullets and fragments. Type 3 (T3) corresponds to 5.6 mm (0.22″) and 7.62–9.65 mm (0.30–0.38″) caliber cartridge cases that were manually collected from the firing points of the 25 and 50 m outdoor ranges. For all types of WAM, the bulk material (roughly 1 kg) was immersed in an ultrasonic bath with HNO_3 1.0% for 10 min, in order to remove the soluble

Table 1
Average chemical composition (% w/w) of different types of waste ammunition material

Element (% w/w)	T1[a]	T2[b]	T3[c]
Pb	99.06	96.38	0.06
Sn	0.01	2.52	0.05
Cu	–	0.12	70.32
Zn	–	0.03	27.91
Sb	0.64	0.83	0.02
Fe	–	0.006	0.03
Al	–	0.004	0.02
Ni	0.01	0.001	0.20
Cr	–	0.001	0.03
As	–	0.01	0.001
Hg	–	0.001	0.004
Bi	–	–	0.001

[a] Type 1 WAM.
[b] Type 2 WAM.
[c] Type 3 WAM.

Table 2
Characteristics of the industrial cement raw mix and the produced clinker

Raw mix		Clinker			
Chemical composition (% w/w)		Potential mineral composition (Bogue) (% w/w)		Moduli	
SiO_2	13.76	C_3S	71.1	LSF[b]	0.981
Al_2O_3	3.23	C_2S	7.7	SM[c]	2.42
Fe_2O_3	2.45	C_3A	6.9	AR[d]	1.32
CaO	43.11	C_4AF	11.6	HM[e]	2.22
MgO	0.55				
K_2O	0.28				
LOI[a]	35.62				

[a] LOI = loss on ignition.
[b] LSF = lime saturation factor.
[c] SM = silica modulus.
[d] AM = alumina modulus.
[e] HM = hydraulic modulus.

impurities (residues from the primer mixture, paper target pieces, dust, soil etc.), rinsed afterwards with deionized water and then dried at 105 °C for 24 h in an laboratory electrical oven. The dried material was ground in a laboratory ultrafine attrition mill, to a particle size <90 μm. The chemical composition of each type of ground WAM was obtained using atomic absorption spectroscopy (AAS) and is presented in Table 1. Ordinary Portland cement raw meal of industrial origin was used (residue at 90 μm: 15%). The chemical composition of the raw mix as well as the mineral composition (according to Bogue) and the moduli of the obtained clinker are presented in Table 2.

2.2. Sampling strategy and preparation

Three different blends of WAM (B1, B2 and B3 respectively) were prepared, by intensively mixing T1, T2 and T3 WAM types in a laboratory swing mill for 1 h, in order to be employed as secondary raw material for clinker production. The selected proportions of T1–T3 used for the production of the three blends, as well as their codification are given in Table 3. Table 3 gives also the composition and sample codification of the modified raw mixtures prepared for this study. One reference and twelve modified mixtures were prepared by mixing the reference sample with 0.5%, 1.0%, 1.5% and 2.0% w/w of B1–B3 WAM blends in a laboratory swing mill for 1 h. Homogeneity was ascertained by dosing the added elements, in some indicative samples.

2.3. Burning procedure

All samples were pressed to form pellets, placed in a Pt-dish and were thermally treated at 1100, 1200, 1300, 1350, 1400 and 1450 °C for 20 min in an electrical furnace and then were rapidly cooled. Sintering and cooling conditions were kept strictly constant.

2.4. Measuring and monitoring techniques

The sintering reactions in all modified raw mix samples were recorded by means of differential thermal analysis using a Mettler Toledo TGA/SDTA 851 instrument. The temperature was raised at a constant rate (10 °C/min) from ambient to 1450 °C. The experiments were conducted in a static atmosphere. The effect on the burnability was evaluated on the basis of the unreacted lime content in samples sintered at the above-mentioned temperatures. The sintered pellets were ground and analyzed by the ethylene glycol method [35,36] in order to estimate the free CaO (fCaO) content in the final sintering products and using a Siemens

Table 3
Codification and mixture compositions (% w/w) of the produced WAM blends and modified raw mixes

WAM Blends	BD1[a]	BD2[b]		BD3[c]
	35% T1, 35% T2, 30% T3	25% T1, 25% T2, 50% T3		15% T1, 15% T2, 70% T3
Raw mixes				
	M1-05	M1-10	M1-15	M1-20
	0.5% BD1, 99.5% OCRM[d]	1.0% BD1, 99.0% OCRM	1.5% BD1, 98.5% OCRM	2.0% BD1, 98.0% OCRM
	M2-05	M2-10	M2-15	M2-20
	0.5% BD2, 99.5% OCRM	1.0% BD2, 99.0% OCRM	1.5% BD2, 98.5% OCRM	2.0% BD2, 98.0% OCRM
	M3-05	M3-10	M3-15	M3-20
	0.5% BD3, 99.5% OCRM	1.0% BD3, 99.0% OCRM	1.5% BD3, 98.5% OCRM	2.0% BD3, 98.0% OCRM

[a] BD1 = blend 1.
[b] BD2 = blend 2.
[c] BD3 = blend 3.
[d] OCRM = ordinary cement raw meal.

D-5000 X-Ray Diffractometer, with nickel-filtered Cu Kα_1 radiation ($\lambda = 1.5405$ Å), in order to identify the mineralogical phases formed during sintering.

The content of the added minor elements in the samples, sintered at 1450 °C, was determined, using atomic absorption spectroscopy (AAS), in order to evaluate the incorporation degree of the main foreign elements in clinker phases. Prior to measurement, 1 g of each sample was dissolved according to Maczkowski method.

Scanning electron microscopy was used in selected samples in order to examine the texture of the obtained clinkers at 1450 °C and the distribution of the foreign elements in their main phases. A JEOL JSM-5600 scanning electron microscope, interfaced to an OXFORD LINK ISIS 300 energy dispersive X-ray spectrometer (EDXS) was used. Experimental conditions involved 20 kV accelerating voltage and 0.5 nA beam current.

2.5. Cement hydration and properties

The clinkers were interground with 5.0% w/w gypsum in a pro-pilot plant ball mill of 5 kg capacity. The gypsum was of industrial origin (98% w/w $Ca_2SO_4 \cdot 2\,H_2O$). The fineness of all the produced cements was found to be in the range between 3500 and 3700 cm^2/g (Blaine). The compressive strength of the samples (EN 196-1) as well as the consistency of standard paste, the setting time and the soundness (EN 196-3) was determined.

The cements were mixed with water in order to prepare cement pastes. A water-to-cement ratio (W/C) of 0.4 was retained for all pastes and deionized water was used. After a period of 6 h the cement cores were put in polyethene containers (vials), sealed hermetically and wet-cured at 20 °C. Samples hydrated for periods of 1, 2, 7, and 28 days were subjected to acetone and isopropyl ether treatment and then dried for 24 h in vacuum. The hydrated samples were ground to pass through a 54 μm sieve and were studied by means of XRD in order to identify the hydrated products. In addition, thermogravimetry analysis (TGA) was used for the evaluation of the hydration rate. The samples were heated from 20 to 600 °C at a constant rate of 15 °C/min in an atmosphere of carbon dioxide free nitrogen, flowing in 50 cm^3/min. A limited number of samples were treated up to 1000 °C in order to find out if there was any carbonation of $Ca(OH)_2$.

2.6. Leaching tests

The procedure used for the leaching tests was the ANSI/ANS-16.1-1986. The leachant was deionized water with a conductivity <6 μΩ/cm in which the specimens, with a volume of leachant to external geometric surface area of the specimen (195 cm^2) ratio of 10 cm, were immersed in individual plastic vials for 1, 2, 7, 28 and 90 days. Plastic vials were kept in watertight containers full of water, which were stored in a curing chamber, thus assuring maximum possible humidity. When leaching time was over, leachates were extracted from the plastic containers and put in refrigerator to avoid evaporation. The concentration of the main heavy metals Pb, Cu, Zn, Sn and Sb (presented in the modified raw mixtures) was determined by induction-coupled plasma emission spectrometry (ICP). pH was kept constant at the range of 7.0 by feed-back control and addition of 0.1 N HNO_3 or 0.1 N NaOH solutions.

3. Results and discussion

3.1. WAM characterization

Although the results derived from chemical analysis of T1, T2 and T3 types concern a waste material that is found in Greece, the basic conclusions are applicable and results of the same magnitude are expected in relevant cases in other countries of the European Union, since the same ammunition types are widely used across Europe and USA for the same purposes. Additional chemical analyses carried out in WAM, collected from the same shooting ranges in different posterior periods, showed a rather consistent composition of the WAM in the main constituent elements.

As it can be seen from the results of Table 1, the addition of T1 and T2 WAM in the raw material will introduce significant quantities of lead as the main foreign element, while T3 will introduce significant quantities of Cu and Zn. In the high oxidizing-high temperature kiln environment most of the heavy metals form oxides. Since Pb exhibits high volatility during sintering, in order to avoid high lead emissions and to enhance the mineralizing effect of Cu, Zn and other trace elements, it was decided to prepare blends of T1–T3 WAM, enriched in T3, and to limit their use in the cement raw meal to fractions that will not exceed 2.0% w/w.

The production of these three blends containing different proportions of Pb, Cu, Zn, Sn and Sb elements is an easy way to fix problems encountered from the variability of WAM chemical composition.

3.2. Thermal studies of modified clinkers

In the DTA curve of a cement raw mix the following stages are distinguished:

- a broad endothermic effect attributed to the dehydroxylation of clays (200–600 °C),
- a strong endothermic effect around 900 °C caused by the decomposition of the limestone,
- one or more exothermic reactions (1200–1350 °C) connected with the belite (C_2S) formation,
- an endothermic reaction just after the last exothermic reaction (1300–1400 °C) associated with the partial melting of the sample.

The first two stages depend on the chemical and mineralogical characteristics of the clay and the limestone respectively, and as it was expected, they are identical in all samples. The most important stages are the third and the fourth which are directly associated with the clinkerization process.

Fig. 1 presents the DTA curves of the pure sample and the modified raw mixes containing 2.0% w/w of the three waste ammunition blends.

The evaluation of the DTA curves of all modified raw meals led to the following remarks:

- In all modified samples the reactions associated with the decomposition of $CaCO_3$ (in the temperature range of 800–900 °C) and clinkerization (1200–1450 °C) are recorded, suggesting satisfactory burning and clinkerization of all samples.
- The added WAM blends do not affect the decomposition of $CaCO_3$ and the belite formation. In all modified mixtures the formation of the melt is shifted to lower temperature and overlapped with the belite formation. This fact indicates that the constituents of the added WAM blends are dissolved in the liquid phase, affecting mainly the formation and the properties of the melt and therefore change the reactivity of the mixture at high temperatures.

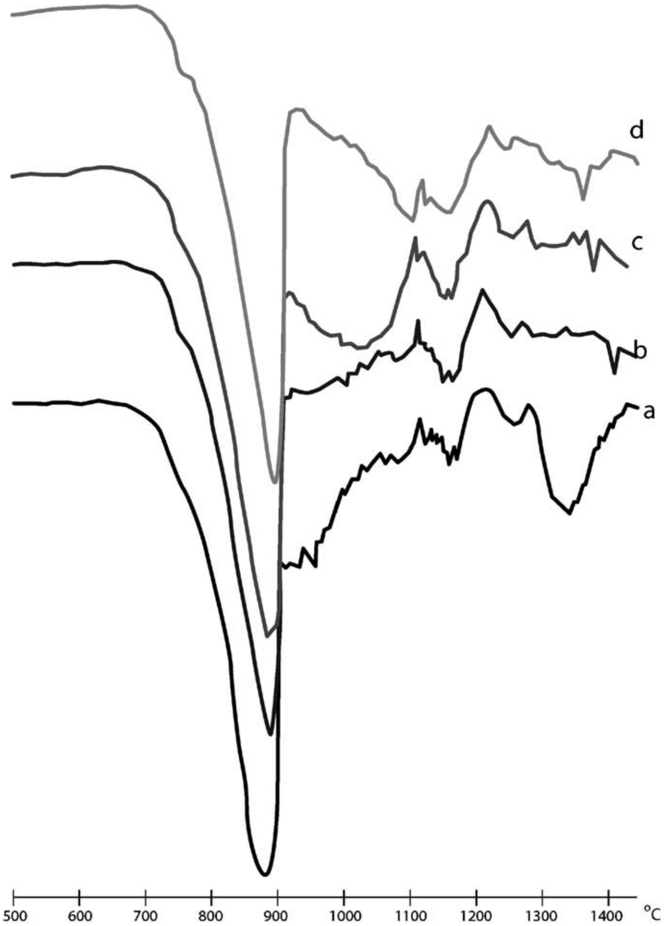

Fig. 1. DTA curves of (a) pure, (b) M1-20, (c) M2-20, and (d) M3-20 modified samples.

3.3. Burnability of the raw mix

The effect of the added WAM blends on the overall burnability of the raw mixtures was evaluated on the basis of the unreacted lime (fCaO) content after sintering at varying temperatures. Table 4 presents the fCaO content in relation to the sintering temperature and the WAM blend content in the modified raw mixes. Using the fCaO values of the sintered samples, the burnability capacity (BC) of the raw mix can be estimated from Eqs. (1) and (2) [37].

$$\begin{aligned} C = {} & 2\text{fCaO}_{1100^\circ C} + 2\text{fCaO}_{1200^\circ C} + 3\text{fCaO}_{1300^\circ C} \\ & + 4\text{fCaO}_{1350^\circ C} + 4\text{fCaO}_{1400^\circ C} + 2\text{fCaO}_{1450^\circ C} \end{aligned} \tag{1}$$

$$BC = 600/C \tag{2}$$

The resulted values of BC are also given in Table 4. The ratio of the burnability capacity of the sintered samples to the burnability capacity of the pure sample, in relation to the doping WAM blend concentration in the raw mix is presented in Fig. 2. BC ratio greater than 1 indicates that the added mineral favors the sintering process.

Table 4
fCaO and BC values of sintered products

Raw mix	fCaO (%)						BC[a]
	Temperature (°C)						
	1100	1200	1300	1350	1400	1450	
Reference	39.71	31.77	14.47	8.62	4.88	1.99	2.46
M1-05	39.67	29.84	13.12	8.10	4.11	1.77	2.60
M1-10	39.41	29.07	12.51	7.61	4.00	1.52	2.68
M1-15	38.72	28.52	11.71	7.52	3.76	1.34	2.76
M1-20	37.70	27.11	10.33	6.81	3.43	1.10	2.94
M2-05	39.51	29.61	12.91	7.67	3.86	1.53	2.65
M2-10	39.11	28.07	12.09	7.02	3.61	1.39	2.78
M2-15	38.41	26.52	9.86	5.85	2.86	0.91	3.18
M2-20	37.10	24.11	8.11	5.12	2.27	0.63	3.52
M3-05	39.07	21.43	11.51	5.55	2.51	1.01	3.16
M3-10	38.21	20.11	10.41	4.31	1.84	0.77	3.45
M3-15	36.70	17.38	6.33	2.15	1.52	0.31	4.31
M3-20	35.10	15.45	5.71	1.58	0.62	0.17	4.72

[a] BC = burnability capacity.

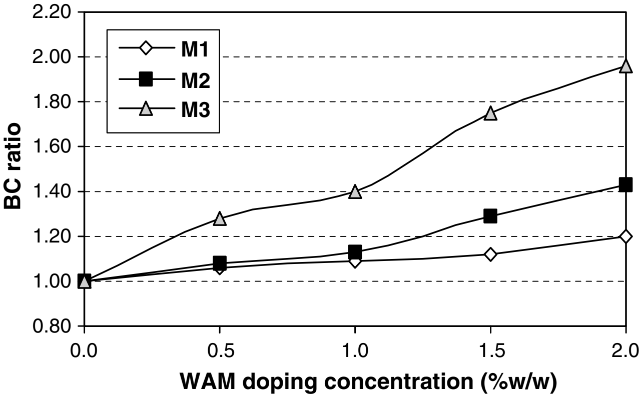

Fig. 2. BC ratio in relation to the waste ammunition material content in the modified cement raw mixes.

As it is seen (Table 4), the addition of the WAM blends in the conventional cement raw meal improves the burnability of the raw mix. Surprisingly, a positive effect is recorded even from 1100 °C, attributed to the presence of Pb, Cu, Zn, Sn and Sb in the raw mix. A significant decrease in the fCaO content is recorded at 1450, 1400 and 1350 °C (by 11–45%, 16–30% and 6–21% in M1, 23–68%, 21–53% and 11–41% in M2 and 49–91%, 49–87% and 36–82% in M3, respectively), implying a remarkable impact of the added blends on the reactions that proceed in the presence of the liquid phase. This is also reflected on the BC values (Fig. 2), which are mainly based on the fCaO content at 1400 and 1350 °C. On the overall, even 0.5% w/w addition of any WAM blend is considered to improve the burnability of the raw mix, even in low temperatures. The positive effect of the waste material seems to be somehow proportional to the doping concentration. Optimum results were achieved in the case of M3 modified raw mixes, followed by M2 and M1, where the Cu and Zn fractions in the raw meal were significantly higher.

There is no previous literature on the effect of Pb, Sn and Sb compounds on the reactivity of the cement raw mix. The mineralizing action of CuO and SnO_2 seems to be related to their incorporation in solid solutions with calcium oxide and/or an acceleration of the reactions among the four main oxides, rather than the decomposition of calcium carbonate. The dark colour of all sintered samples, even at 1100 °C, indicates a high degree of combination of the main constituents and especially of Fe_2O_3. Previous study by the author reported improvements in the reactivity of the $CaO–SiO_2–Al_2O_3–Fe_2O_3$ system, already at 1100 °C, by the addition of 1.0% w/w CuO in the synthetic raw mix [18]. In fact, Odler and Abdul-Maula [38,39] as well as Kakali et al. [31] have found CuO to be an efficient mineralizer and flux at 1450 °C, but in a lesser extend, compared with 1200 °C. ZnO is acting both as mineralizer and flux, by accelerating clinker formation, leading to higher activity and promoting the solid reactions as well as the formation of alite by increasing the amount of liquid phase [32–34].

3.4. Incorporation degree of the minor elements in clinker

The incorporation degree of the added foreign elements Pb, Cu, Zn and Sn was obtained by comparing the theoretical content with the data from the chemical analysis in samples sintered at 1450 °C. The theoretical content was calculated using the data from the chemical analysis of the T1–T3 WAM types and the ordinary cement raw meal, taking into account the measured loss on ignition (LOI). Results are given in Table 5.

Table 5
Incorporation degree (%) of Pb, Cu, Zn and Sn in clinker

Sintered sample	Incorporation degree (%)			
	Pb	Cu	Zn	Sn
M1-05	41.8	100.0	100.0	100.0
M1-10	37.1	100.0	98.4	100.0
M1-15	36.3	98.9	97.5	100.0
M1-20	28.6	99.4	94.2	99.4
M2-05	53.1	97.6	95.3	100.0
M2-10	48.3	98.2	91.1	99.5
M2-15	45.9	95.3	90.0	99.3
M2-20	43.7	90.3	86.2	99.7
M3-05	60.2	93.3	89.1	99.9
M3-10	56.2	90.1	82.8	99.6
M3-15	57.3	85.8	77.6	99.1
M3-20	55.6	83.9	73.3	98.9

The contents of lead measured in M1–M3 clinkers show an average incorporation degree of 46%, with a maximum of 60%, a value that should be considered high, in comparison to relative published data [26–30]. As lead content decreases from M1 to M3 samples, the incorporation degree for lead seems to be stabilized. On the other hand the incorporation degree for copper and zinc fluctuates between 84–100% and 73–100% respectively. Tin and antimony seem not to be volatilized at all.

It must be noted that the thermal treatment of the samples was performed as a batch operation in a laboratory electrical furnace. In industrial practice the evaporation of heavy metals depends on the composition of the raw meal, burning conditions and atmosphere (oxidizing or reducing) during the burning process. Even though in many cases the presence of alkalies or chlorine in industrial raw meals increases the volatility of certain elements that form volatile chlorides or alkali salts which participate in the so-called alkali cycle, their retention within clinker phases depends upon the process type and the extent to which precipitator/bag filter dust is returned to the kiln. Thus, in a suspension preheater kiln with nearly 100% return of dust to the kiln and a dust collecting system meeting current environmental requirements, an almost complete retention of such elements could be accomplished.

3.5. XRD studies of modified clinkers

All samples sintered at 1450 °C have the structure of a typical clinker. The dominant phases (alite, belite, calcium aluminate and ferrite) were well crystallized, giving peaks at the common 2θ values. Additionally, no detection of undesired compounds (γ-C_2S) was recorded. Differentiations among samples were restricted in calcium aluminate and ferrite, due to the selective incorporation of the constituents of the WAM blends in these phases and the changes that occur in their chemical composition and structure. Indications concerning the formation of $PbSiO_3$ phase were recorded in clinker matrices sintered at 1450 °C that correspond to M1 and M2 raw mixtures, enriched in B1 and B2 WAM blends. Similar indications concerning the partial formation of the compound $CaCu_2O_3$ were also recorded in the XRD patterns of samples doped with more than 1.0% w/w of the B3 WAM blend.

3.6. SEM studies of modified clinkers

SEM studies were conducted in order to examine the structure of selected clinkers obtained and the distribution of the foreign elements in their main phases. The doping concentration of 2.0% w/w was chosen in order to strengthen the effect of the added foreign elements on the structure of clinker and facilitate their detection by SEM in the clinker compounds. The SEM observations are summarized in Table 6, while the SEM photos of the pure and modified clinkers originated from raw mixes doped with 2.0% w/w B1, B2 and B3 WAM blends, burned at 1450 °C, are given in Fig. 3. Codification for clinkers simply follows the codification for the corresponding modified raw mixes.

The photos were selected to be representative as far as the size and the shape of alite and belite crystals are concerned. With the spot analysis of EDXS, the composition of the principal phases was analyzed at five to eight points. Owing to instrumental limitations, accuracy in analyses of the minute grains in the interstitial phases proves difficult to achieve. In any case, the comparison of the spot analysis in each clinker phase can lead to only qualitative indications concerning the distribution of the minor elements in the individual clinker compounds.

From Fig. 3 it is concluded that the addition of the three WAM blends results in variations in the appearance of both alite and belite crystals that seem to be enhanced as the raw mix is enriched in Cu and Zn. Alite was developed in large compact crystals, which tend to appear more prismatic and angular in shape, especially as the doping concentration of Pb is lowered (M2-20 and M3-20 sintered samples), in contrast to the slightly angular hexagonal outline of C_3S grains in reference and M1-20 samples. Belite as well was uniformly distributed, forming bigger in size and rounded in shape crystals. The amount of interstitial matrix in all tested samples was generally adequate, having a fine-crystalline structure.

In contrast to Pb, which was preferentially found in the silicate phases (especially in alite), EDXS analyses showed

Table 6
Size and shape of alite and belite crystals in modified clinkers

Sintered sample	Alite		Belite	
	Size (μm)	Shape	Size (μm)	Shape
Reference	20–30	Compact, prismatic, with slightly rounded outline	5–10	Small, roundish
M1-20	30–40	Larger in size, compact, rounded at the rims	5–10	Round
M2-20	40–60	Compact, prismatic, with slightly angular hexagonal outline	5–15	Bigger in size, round
M3-20	40–60	Angular, rather elongated, prismatic	5–15	Bigger in size, round

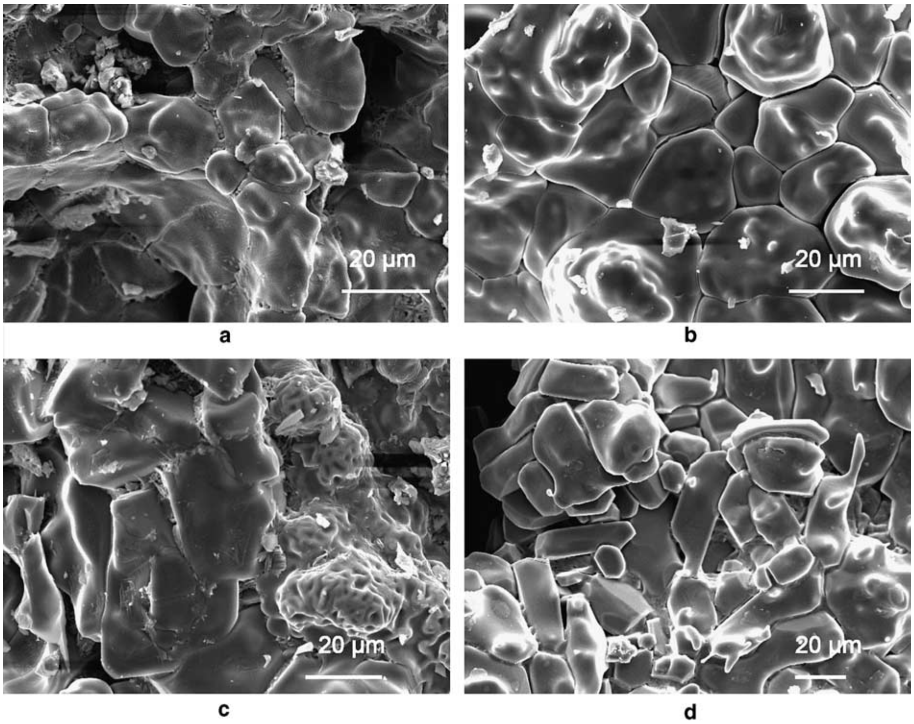

Fig. 3. SEM photos of (a) pure, (b) M1-20, (c) M2-20, and (d) M3-20 modified clinkers.

that Cu, Zn, Sn and Sb are selectively incorporated in the interstitial material, as their doping concentration in the modified raw mixtures is increased. EDXS analyses performed on selected spots at the rims of alite crystals indicated a high Pb and Si content ($PbO:SiO_2$ approximately equals 1:1) in M1-20 sintered sample and a high Cu and Ca content (CaO:CuO approximately equals 1:2) in M3-20 sintered sample, also seen in the XRD patterns of that particular samples. However the low content of $PbSiO_3$ and $CaCu_2O_3$ compounds and the overlapping of the clinker peaks do not permit a safe identification.

3.7. Hydration rate of cement pastes

All pastes were studied by means of a TG analyzer. The weight loss up to 550 °C, which corresponds to the total water incorporated in the cement paste, was determined. The $Ca(OH)_2$ content, which is directly related to the hydration of silicate compounds, was also measured. The weight loss in the range 600–700 °C, if any, corresponds to the decomposition of $CaCO_3$ and it has to be converted to the equivalent $Ca(OH)_2$ and then to equivalent H_2O. The carbonation of the pastes may take place during the preparation of the paste or during the grinding of the paste previous to the TG measurement. The water combined in the hydration products (other than calcium hydroxide) corresponds to the weight loss up to 300 °C. Any changes of this amount indicate that the kind and/or the stoichiometry of the hydration products are changed.

Table 7 presents the content of the total compound water, calcium hydroxide and water in the hydration products in the case of C3 pastes (originated from M3 clinkers), in relation to the age of hydration.

Table 7
Total compound water, calcium hydroxide and water in the hydration products, in relation to the age of hydration for C3 cement pastes

Cement paste	Hydration age (days)			
	1	2	7	28
	Compound water (% w/w)			
–	15.47	17.97	16.90	23.55
C3-05	17.10	16.69	18.75	24.88
C3-10	15.44	15.55	18.01	23.88
C3-15	14.36	14.92	17.33	22.72
C3-20	14.02	15.63	16.75	22.35
	$Ca(OH)_2$ (% w/w)			
–	20.39	21.49	24.21	26.68
C3-05	20.56	17.02	23.93	24.98
C3-10	19.61	18.75	23.39	24.17
C3-15	18.64	20.51	23.53	23.76
C3-20	16.03	19.45	21.72	23.27
	Water in hydrated products (% w/w)			
–	10.51	12.74	11.01	17.06
C3-05	12.10	12.55	12.93	18.80
C3-10	10.67	10.99	12.32	18.00
C3-15	9.82	9.93	11.61	16.94
C3-20	10.12	10.90	11.47	16.69

As it was extracted from the evaluation of the TG tests, small additions of the added B1–B3 WAM blends (up to 1.0% w/w) do not significantly affect the total rate of hydration. As the waste material content in the raw mix increases, the hydration tends to slow down, as it is indicated by the progressive decrease of water and calcium hydroxide content in all pastes. The stronger effect of the added materials on the calcium hydroxide content indicates that they affect especially the hydration of silicate compounds. When heavy elements, such as Pb, Cu and Zn, are present in cement, the early hydration reactions are inhibited, probably through the formation of amorphous compounds that cover the unreacted cement grains. The hydration reactions start again after the crystallization and sedimentation of these compounds, a phenomenon that takes place when the Ca^{2+} and OH^- concentration becomes high enough [40–42]. The hydration process, however, of cements produced by clinkers containing the above elements is different, since their incorporation in the crystal lattice of clinker minerals delays their dissolution rate during hydration.

3.8. XRD studies of hydrated samples

In all samples, a gradual increase of $Ca(OH)_2$ content, accompanied by a corresponding decrease of the anhydrous calcium silicate compounds was observed. The formation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), which is the first reaction product between calcium aluminates and gypsum, is confirmed in all samples even after 1 day of hydration. Differentiations are observed after the age of 2 days. The transformation of ettringite to the monosulfate salt ($Ca_4Al_2SO_{10} \cdot 12H_2O$) seems to be delayed, proportionally to the percentage of each WAM blend addition in the raw meal. The most likely reason for the delay is the reduced rate of hydration of the aluminate phase. This extends the period of time required to exhaust the $CaSO_4$ supply. The monosulfate was initially detected in the pure and the 0.5% w/w doped samples after 2 days of hydration, in the 1.0% and 1.5% w/w doped samples after 7 days and in the 2.0% w/w doped sample after 28 days. The rest of the calcium silicate and calcium aluminate hydration products do not present distinct peaks due to their low degree of crystallinity and/or their small amounts.

3.9. Cement properties

Table 8 presents the compressive strength development and setting time of the produced cements in relation to the content of the added blends of waste material.

The cements prepared from the corresponding modified clinkers present almost the same initial strengths (1 day), while a positive effect is observed at 2, 7 and 28 days. From all cement samples studied, those that came from B3 blend presented a higher strength development than the reference one. The 1.0% w/w addition seems to have the optimum effect in all three cement types, while in higher percentages

Table 8
Compressive strength development (N/mm^2) and setting time (min) of cements in relation to the percentage of the added waste ammunition material blends

Sample	Compressive strength (N/mm^2)				Setting time (min)	
	Age (days)					
	1	2	7	28	Initial	Final
Reference	14.6	23.0	38.9	53.3	95	145
C1-05	14.6	23.2	39.4	53.9	97	152
C1-10	14.9	23.6	40.8	54.5	101	156
C1-15	14.7	23.3	40.0	54.1	112	165
C1-20	14.3	24.4	39.9	53.9	118	167
C2-05	14.1	23.5	39.5	54.0	97	141
C2-10	14.9	24.7	40.5	54.9	100	146
C2-15	14.4	24.5	39.7	54.8	106	152
C2-20	14.3	24.3	38.6	54.4	110	161
C3-05	14.4	26.1	42.2	55.1	90	143
C3-10	15.0	28.3	43.7	57.8	95	151
C3-15	14.7	27.1	42.4	56.5	99	157
C3-20	14.7	26.4	41.9	55.8	104	160

of addition (1.5% and 2.0% w/w) the positive effect seems to be inhibited.

The addition of the WAM blends leads to a slight increase of the setting time proportionally to the WAM blend content. This may be due to formation of insoluble Pb, Cu and Zn hydroxides that probably act as retarders during the hydration process by coating the silicate grains and prevent further hydration.

The addition of the secondary waste materials has no effect on the water demand of the cement paste. The standard consistency of all pastes varies from 25.9% to 26.5% in all samples.

The soundness of the tested cements was satisfactory. The expansion measured according to Le Chatelier method varies from 0.8 mm to 1.9 mm while the limit according to EN 197-1 is 10 mm.

3.10. Leaching tests

Table 9 presents results obtained from the leaching tests. It is confirmed that the clinker matrix is capable of stabilizing Pb to a great extent, since concentrations of such element found in leachates are in the range of parts per billion (ppb). Similar to that, very little Cu, Zn and Sn are found in the leaching solutions, even in the age of 90 days. No antimony, mercury, cadmium, chromium, arsenic or bismuth were detected in the leachates corresponding to cements with the highest WAM blend doping addition (2.0% w/w), in all ages. The above behavior is attributed to the high degree of incorporation of the added heavy metals in the crystal lattice of clinker minerals and the delay of their dissolution rate during hydration.

4. Conclusions

The disposal of waste ammunition materials deriving from recreational shooting and/or military activities should be considered as a serious problem. The well-known and generally used methods for waste disposal such as open dumping and landfilling present various disadvantages. With the present technique, almost all quantities of spent ammunition can be incorporated into the raw materials for the manufacture of Portland cement clinker with practically complete elimination of toxic impact in environmental matrices during disposal and without affecting the quality of the final cement product. The waste ammunition blends may be used successfully as a secondary raw material for partial substitution of the conventional raw materials, leading to resources conservation and ensuring the quality of the produced cement.

Table 9
Concentration (mg/l) of Pb, Cu, Zn and Sn in leachates

Paste	Hydration age (days)					Hydration age (days)				
	1	2	7	28	90	1	2	7	28	90
	Pb (mg/l)					*Cu (mg/l)*				
C1-10	0.039	0.043	0.076	0.150	0.197	n.d.[a]	n.d.	0.011	0.023	0.021
C1-20	0.063	0.099	0.165	0.223	0.245	0.011	0.019	0.016	0.033	0.042
C2-10	0.022	0.033	0.049	0.099	0.140	n.d.	n.d.	0.015	0.029	0.040
C2-20	0.046	0.068	0.076	0.124	0.176	n.d	0.018	0.037	0.047	0.059
C3-10	0.012	0.017	0.028	0.039	0.087	0.011	0.017	0.028	0.039	0.087
C3-20	0.022	0.033	0.051	0.091	0.111	0.011	0.033	0.051	0.091	0.131
	Zn (mg/l)					*Sn (mg/l)*				
C1-10	n.d.	n.d.	n.d.	0.011	0.016	n.d.	n.d.	n.d.	0.014	0.017
C1-20	n.d.	n.d.	n.d.	0.015	0.023	n.d.	n.d.	n.d.	0.015	0.029
C2-10	n.d	n.d	0.016	0.024	0.029	n.d.	n.d.	n.d.	n.d.	0.015
C2-20	n.d.	n.d.	0.019	0.031	0.042	n.d.	n.d.	n.d.	n.d.	0.019
C3-10	n.d	0.010	0.018	0.041	0.063	n.d.	n.d.	n.d.	n.d.	n.d.
C3-20	0.010	0.019	0.020	0.066	0.072	n.d.	n.d.	n.d.	n.d.	n.d.

[a] n.d. = not detected.

From the present study the following conclusions can be drawn:

- The addition of the waste ammunition material promotes the consumption of free lime and improves the burnability of the raw mix, especially during the final stage of the sintering. This positive effect is proportional to the doping concentration.
- The contents of lead measured in the modified clinkers show an average incorporation degree of 46%, a value that should be considered high, in comparison to relative published data. Almost all amounts of Cu, Zn, Sn and Sb in the modified raw mixes are retained in clinker.
- Except from Pb, which was preferentially found in the silicate phases, Cu, Zn, Sn and Sb are mainly concentrated in the melt, affecting the growth environment of alite crystals and modifying their shape and size.
- Despite the slight retarding effect on the hydration process, the added waste ammunition blends improve strength development and do not affect the physical properties of the cements. Optimum results were obtained in the case of the Cu and Zn enriched blend, in the doping concentration of 1.0% w/w.
- The fixation of the heavy metals, present in the waste ammunition material, in the clinker minerals, led to considerably low concentrations detected in the leachates for all ages tested.

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