"POLITEHNICA" UNIVERSITY of BUCHAREST

DOCTORAL SCHOOL

APPLIED CHEMISTRY AND MATERIALS SCIENCE

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THESIS

SUMMARY

Inertization of wastes in binder matrices

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BUCHAREST 2021

Content

Keywords:

"*Waste*" - any substance or object that the owner discards or has the intention or obligation to discard according with Decision nr. 349 from 21 april 2005.

"*Hazardous waste*" - any waste having one or more of the hazardous properties listed in Annex no. 4 of the law (Decision nr. 349 from 21 april 2005).

"*Co-processing*" - the activity that ensures the inertization of waste by embedding it in the binder matrix, recycling waste by replacing raw materials or additives, and energy recovery by substituting fossil fuels.

"*Inertization*" - The process by which harmful elements in certain wastes interact with components of binder matrices (either by isomorphic addition to the structure of mineralogical phases in the clinker; or by the formation of insoluble salts in the operating environment) leading to their lack of reactivity of other elements or other substances, so as to achieve the desired mechanical properties while inhibiting the harmful actions that are characteristic of heavy metals.

"*Clincher*" – Intermediar product obtained in the manufacture of cement by heating the raw material to close to the vitrifying temperature and by transforming it into a compact and hard mass.

"*Portland Cement*" – A building material in the form of a fine powder, obtained by grinding the clinker and which, in contact with water, sets and hardens.

"*Puzzolanic materials*" – Natural materials of siliceous, silico-aluminous composition or a combination of those two, that contain silica and alumina with a low degree of crystallinity and are characterized by a high reactivity.

"*By-product*" – means a product (usually waste or recoverable substance) obtained from the same manufacturing process as the basic product; by-product

"*Correction additives*" – wastes used to obtain cement that meet certain characteristics.

"*Cement additives*" – waste used in cement, which does not affect the physical-mechanical and structural characteristics of the binders obtained.

"*Landfill*" – a site for the final disposal of waste by landfill or underground, inclusive.

"*Leached*" – the leachate (solid particles suspended in aqueous medium) or sludge (pumpable) resulting from the drainage system of a landfill.

"*Treatment of leachate*" – the process or sequence of physico-chemical and biological processes by which the values of indicators characteristic of leachate are brought within limits to allow its evacuation into sewers or natural receptors.

"*Instalation for the leachate treatment*" - all the machinery and equipment in which the physical-chemical and / or biological treatment processes take place.

Chapter 1. Wastes used in the cement industry

1.1. Legislative aspects regarding the use of waste in the cement industry

In our country, law no. 211/2011, republished in 2014, establishes the necessary measures for the protection of the environment and the health of the population, by preventing or reducing the adverse effects caused by waste generation and management and by reducing the general effects of resource use and increasing the efficiency of their use [9].

Developed countries no longer consider waste storage and incineration as viable long-term solutions. Both variants have specific disadvantages and rather consume instead of conserving valuable resources. Municipal waste storage consumes large areas of land, min. 80 km2 are consumed every year. Another 13 million tonnes of incineration waste are deposited annually. As a result, multinational companies are increasingly adopting policies to completely eliminate landfilling and reduce their carbon footprint.

One such solution is the co-processing of waste. The co-processing activity ensures the inertization of the waste by incorporating it in the binder matrix, the recycling of the waste by replacing raw materials or additives, as well as the energy recovery by substituting fossil fuels. Organic pollutants from materials fed in the clinker oven are completely destroyed in the high temperature zone, and ash is included in the final product [54-55].

1.2. Characteristics of waste used to obtain clinker and cement - as raw materials; alternative fuels; additives to grinding

In order to ensure the stability of the parameters followed according to the legal requirements and product compliance, the waste that enters the cement production process and can affect its quality, is carefully controlled from a physico-chemical point of view [56]. The quality control process covers the whole chain: from the process that generates the waste, the quality control of the waste sent to co-processing, the technological process of obtaining the cement, the control of the manufacturing recipe, the control of stack emissions, the quality control of the final product.

The basis for the use of waste and the appropriate control system are clearly defined in the specifications of cement plants. The specifications must comply with the specific requirements of cement plants and regulatory requirements (legal requirements).

Specific requirements for cement plants - are established in accordance with the 'Pollution Prevention and Control' (IPPC) and plant properties that have a significant impact on the operation of the plant and the quality of the delivered product.

Regulatory requirements - establish the properties of waste, which can have an impact on human health and safety and the environment.

In order to be considered as a corrective addition to the clinker used or as a secondary raw material, the waste must meet the following characteristics:

• sum of oxides (Al_2O_3, Fe_2O_3, SiO_2, CaO, SO_3)> 60%;

• granulometry <40mm, humidity <20%, volatile emissions 0 mg / kg, chlorine content <0.5 mg / kg, sulfur content <10mg / kg, PCB / PCT <50 mg / kg, Na_2O <1%, K_2O <1.5%, P_2O_5 <0.5%, sum of heavy metals (Sb, As, Co, Pb, Cr, Ni, V, Sn, Mn) <1%.

In order to be considered as cement additives, when grinding Portland cement clinker, the waste must not affect the physical-mechanical and structural characteristics of the binders obtained from these additive cements.

1.3. Technological implications for the use of waste in the cement industry

From the point of view of the technological implications that waste has in the cement industry, they are analyzed especially to protect the combustion instalation, because both the combustion process and the quality of the clinker obtained can be affected [67 - 68].

As sources of volatile elements (S, Cl, K, Na) that lead to a circuit inside of the combustion instalation (kiln and heat exchanger) with negative effects on the clinker are:

1. raw materials
2. fuels

These volatile elements can bind in different forms. These combinations are formed as a function of temperature and vapor pressure. Fuels must be properly prepared and homogenized, their dosing and supply must be strictly controlled.

These things must be taken into account to ensure the proper operation of the combustion (flame shape, burner alignment and setting, etc.) [71-74]. Keeping sulfur volatility low is also imperative in order to have the necessary oxygen rate in the kiln, a certain shape of flame, etc. [75].

If we talk about the technological effects of gases resulting from the combustion of fuels, the deposition of phases with a high content of chlorine or sulfur can cause blockages in the heat exchanger, thus causing disturbances in the supply and operation of the kiln [69; 76-82].

Chlorine and sulfur seep into refractory bricks inducing their corrosion. The use of alternative fuels leads to the enrichment with heavy metals of refractories in the upper transition zone (melting zone, where temperatures are between 1200 - 1450 ° C) [69-70].

Chapter. 2. Waste inertization in inorganic binder systems

2.1. Legislative aspects regarding the inertization of waste in binder matrices

The evaluation of the quality of cement and concrete in terms of environmental impact is also based on the dissolution characteristics of heavy metals in water and soil.

The analysis of the toxic elements existing in the concrete in the form of traces is made following the extraction through a controlled diffusion process within pH limits relevant for the environment [110]. Not all metals have the same dissolution characteristics.

There are no constant and simple correlations between the quantities of extracted elements and their total concentration in concrete or cement, therefore, we cannot use the quantities of heavy metals in the eluate as an environmental protection criterion [121-124].

The same legislative aspects that are considered in the cement industry are also taken into account in the case of inertization of waste in binder matrices, namely compliance with environmental regulations regarding leachate, so soil pollution and also water pollution. These reglementations have been described above and are contained in Order 95 [125-128].

2.2. Types of binder matrices used for waste inertization

The binder matrices used for waste inertization are either based on Portland cement or complex systems containing pozzolanic materials.

INERCEM is a range of special hydraulic binders, in the form of a complex, homogeneous mixture, consisting of main constituents - Portland cement clinker, active calcium oxide, and other minor constituents, according to recipes specially adapted exclusively to waste management applications. The commercial special binder range INERCEM type contains several components, depending on the type of waste to be treated, such as: INERCEM C; INERCEM D; INERCEM E; INERCEM A [129-130].

2.3 Interaction processes. The influence of waste on hardening processes

In Portland cement-based binder systems the main hidratated phases are calcium hydrosilicates, portlandite and sulphated calcium hydroaluminates (etringite - Aft; monosulfate - Afm). The

AFm and AFt phases are two hidratated phases that occur when hydrating the binder with tricalcium aluminate content and sulfate source (eg gypsum) [131-135].

Calcium hydrosilicates and portlandite result from hydration of calcium silicates.

Etringite is trisulfated calcium hydroaluminate - $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ (AFt), which is in the form of large, well-formed acicular / prismatic crystals. If its formation takes place at short periods of hardening, then it contributes to the increase of mechanical strength by filling the pores or microcracks in the binder matrix.

Monosulfate is monosulfate calcium hydroaluminate - $C_3A \cdot CaSO_4 \cdot 12H_2O$ (AFm), which is formed in the later stages of hydration, a day or two after mixing, usually by decomposition of etringite.

Setting and hardening process of the cement can be accelerated or slowed down, in accordance with some practical requirements using certain chemicals, in a proportion of 3-5%.

Heavy metal ions, during hydration / hydrolysis processes, may behave differently. Thus, some may form low solubility hydroxides during hydration, thus delaying hydration reactions, some may form more soluble hydroxides, behaving as accelerators of cement hydration. The delay in hydration was attributed to the reduction of permeability due to these products, namely the formation of colloidal metal gels, insoluble precipitates, on the surfaces of cement granules [144].

Heavy metals delay the precipitation of portlandite due to reduced pH resulting from hydrolysis of heavy metal ions during hydration of alite. Heavy metal ions can form co-precipitate with calcium ions in the form of double hydroxides.

Chapter 3. Motivation and objectives of the study undertaken

3.1 Motivation of the study

Detailed explanation of at least 5 aspects related to the inertization and immobilization of some waste, namely:

1. which are the binding matrices that give the best results in terms of inertization and immobilizing harmful / heavy elements;

2. which are the advantages / disadvantages of using various binding matrices;

3.what are the mechanisms of interaction between heavy metals and the compositional characteristics of binder matrices;

4. what types of waste can be inerted in this way, in what proportions, their effects on the properties of the binders;
5. the effects involved in the environment of use of mortars / concretes in which the binder matrix has been inerted and immobilized by solidification / stabilization of waste.

3.2 Research objectives

The objective of this paper was to study the possibility of inertization and immobilizing some waste in inorganic binder matrices based on Portland cement, as well as studying their influence on hydration-hydrolysis processes and the properties of mortars made from these cements.

Chapter. 4. Materials and methods of analysis

4.1. Materials used in the study

We have used the followings:
1. Binder matrices either based on Portland cement or complex systems containing puzzolanic materials, including INERCEM, which is a range of special hydraulic binders.
2. As corrective additions to obtain the clinker (heavy ash resulting from the combustion of petroleum products, in a process of obtaining thermal and electrical energy).
3. In addition to the grinding of Portland cement clinker - (ash resulting from the burning of coal in the industry of obtaining pall panels).
4. A waste rich in chromium from the manufacturing industry of potassium dichromate
5. A leachate from a landfill, collected and passed through a reverse osmosis treatment plant, using various types of ash and special cements.

4.2. Methods of analysis used

1. In order to determine the chemical and mineralogical composition of waste and binder materials were used:
- X-ray diffraction coupled with Rietveld analysis
- X-ray fluorescence spectrometry
- complex thermal analysis
- IR spectroscopy
- potentiometric titration

2. Morphostructural and elemental characteristics of both materials used and hardened binders over different periods of time

- scanning electron microscopy analysis

3. The dispersion characteristics of the materials used were assessed by:

- determination of their specific area (Blaine methode)
- the water needed to prepare pasta of normal consistency
- the setting time being
- mechanical resistance (compression and bending)

4. To determine the quality of the inertization, the following were used:

- optical emission spectrometry, with inductively coupled plasma

Chapter. 5. Waste recovery in the cement industry

5.1 Waste valorification in the cement industry as a raw material

In the study, it was used as a corrective additive in the mixture of raw materials to obtain a Portland clinker, a heavy ash, resulting from a process of obtaining thermal and electrical energy.

Due to the sometimes small specific surface area of heavy ash, it is necessary to grind it. Taking into account their physico-chemical characteristics, heavy ash is generally dosed and added in the raw material grinding stage as part of the raw material mixture [173-175]. Heavy ash (from the base of the kiln) (HA) comes from a power plant where a solid fuel is burned, mostly petroleum coke.

In our study, heavy ash was used as an alternative raw material in the production of Portland clinker. The main characteristics of this clinker were also evaluated in comparison with those of a clinker obtained by burning under the same conditions of an ordinary mixture of raw materials with the same composition.

The two Portland clinker samples were obtained by burning at 1450 ° C a homogeneous mixture of clay and limestone with / without the addition of ash. As the ash sulphate content is high, the degree of substitution in the crude mixture was limited to 4%. The ash had a density of 2.71 g / cm3 and a specific surface area of 3000 cm2 / g.

Following the compositional determinations, 3 potential hazards were identified in the limited use of this material as an alternative raw material in obtaining clinker: 1) high content of vanadium, 2) sulfur and 3) the presence of carbon (resulting from the existence of fractions total burn).

Morphologically, electron microscopy images on ash show ash spheres covered with a loose layer, most likely of calcium carbonate, as well as formations with the appearance of solidified melt, which may be, for example, carbon.

It was observed that in the case of clinker B, the free lime content is similar to that of clinker A, and the content in C3S is approximately equal to that of clinker A, in which the ash was not used as a correction additive. These results corroborated with a similar amount of C2S confirm the same good kinetics of chemical processes that take place during heat treatment and especially the conversion of C2S to C3S [178-179].

Also, by chemical tests, according to the standardization norms, the quantities of minority compounds were determined. There is a very low content in them, especially in free CaO.

From the point of view of the content in heavy elements, X-ray diffraction analyzes with fluorescence were performed, which showed that in both clinker samples they have values in accordance with those reported in the literature [180-185].

From the point of view of grinding aptitude, clinker samples show the same grinding aptitude; the specific surface area of Blaine and the particle size distribution for both cements are approximately the same.

The value of water of normal consistency is approximately the same for both cements. The setting times are identical. Regarding the mechanical properties, at the initial hardening periods there are very small differences which attenuate with the increase of the hardening period.

No major differences were identified regarding the oxide and mineralogical composition of the two clinker samples with or without the addition of ash as a corrective material.

5.2 Waste valorification in the cement industry as an addition to grinding

Thermal power plant ash is a by-product resulting from the burning of coal in thermal power plants to produce electricity, it is used in cement plants as an addition to grinding Portland cement clinker to a maximum of 35% [195-196]. According to the literature [197-201] it has been found that the substitution of cement with power plant ash leads to a decrease in mechanical strength at short curing times (up to 28 days), but will contribute to increased mechanical strength at longer periods of hydration and, implicitly, to increase the durability of that structure.

Based on this information, the present paper has studied the influence of substituting Portland cement (CEM I 52) with a light ash (Krono), resulting in obtaining the pallet, at a temperature lower (over 800 ° C) than the temperature of obtaining the power plant ash (above 1100 ° C), on the curing processes and properties of the respective binders. This coal-burning ash - light ash, contains as main oxides: lime (CaO), silica (SiO2) and alumina (Al2O3).

For this study, mixed binder masses were made in which the substitution of Portland cement with Krono ash was 5, 10, 15 and 20%.

The aim was to stabilize the ash in the reinforced binder system in a more stable physical and chemical form, so less toxic and / or less mobile. This stabilization involves complex interactions in the ash - mineralogical phases of the cement - water system.

The use of this light ash from the manufacture of the pallet as an addition to the grinding of Portland cement clinker, dosed by its substitution, has led to characteristic binding properties that make it possible to use such mixed binders in practice.

The hydration-hydrolysis processes are slowed down by the increase of the ash content due to the dilution of the cement.

It was observed that the value of water of standard consistency increases with increasing degree of dilution of CP with CK, most likely due to the morphological characteristics of the ash (has the ability to absorb water) and changes in dispersion characteristics (high fineness of ash increases an increase in fineness binder mixtures containing CK).

It was observed that the uptake time increases with increasing CK content; for example, the setting time for the binder mass with a content of 10% CK-M2, is 3.5 times longer than for the sample without CK-E. .

For a degree of substitution of 10% of Portland Cement with Krono Ash, the best values of mechanical strength were obtained, the nature of the hydration phases being similar to that of hydrated Portland cement. These data are also confirmed by the existing data in the literature [209-215].

Also, low-intensity interferences for calcium hydrosilicates (JCPDS 72-0156) and the AFm-type monosulfate phase formed at longer curing periods by the Et transformation were highlighted.

From a microstructural point of view, they highlighted for all masses the morphologies characteristic of the hydration phases: hexagonal platelets characteristic of portlandite; fine needle formations and wrinkled foils characteristic of calcium hydrosilicates; larger acicular crystals characteristic of etringite; thin hexagonal platelets placed plane-parallel characteristic of the monosulfate phase.

Chapter 6. Chromium-rich industrial waste inertization in different types of binder matrices

6.1 Waste inertization into Portland cement-based binders with various additives

For this study, the inertization and immobilization of a chromium-rich waste from the potassium dichromate manufacturing industry, in Portland cement-based inorganic binder matrices, as well as the study of its influence on hydration-hydrolysis processes and mortar properties were considered. made on the basis of these cements. The following classes of cements were used:

• Portland cement for industrial production type CEM II / A-M (S-LL) 42.5R;

• Portland cement for industrial production type CEM II / A-L (LL).

The binder compositions obtained on the basis of the chromium-rich waste and the two cements are given in table 3, the waste being dosed so as to bring 0.5 and 1% chromium (% grav.).

It was observed that with the increase of the proportion of waste, the value of water of standard consistency increases, this being in close correlation with the values of specific surface. The setting time depends significantly on the proportion of waste, the characteristics of the Portland cement - composition, fineness of grinding, as well as the amount of water of standard consistency. It can be estimated, based on the determination of setting time, that the waste delays the setting time compared to the standard, in correlation with the hydration processes and the formation of hydrocompounds.

Developed mechanical strengths increase over time; the presence of waste, in certain proportions in the studied binder systems, determines diminutions of the mechanical resistances that they develop in time; the decrease in mechanical strength is all the more pronounced the higher the proportion of waste.

In general, the intensities of calcium hydroxide increase over time, being significantly lower for waste masses, which may be a consequence of the dilution of cement by the addition of waste or as a result of the delayed effect due to waste on the hydration - hydrolysis process; the decrease in calcium hydroxide content for cement-based binders with cement C with / without added waste hardened for 90 days can be explained by its carbonation, being in good accordance with the diffractograms in figure 6.8. Etringitis is formed from 2 days of hydration. Its evolution over time is discontinuous, due to its partial transformation into the monosulfate compound. The monosulfate is detected by low intensity lines, which makes it difficult to detect

X-ray (in the 90-day C0-hardened paste it is observed that the lines characteristic of etringite disappear, and the characteristic lines of monosulfate do not appear).

It has been observed that the loss in calcination of L-type masses is higher than that of type C, which shows a better interaction with water due to a higher fineness.

The calcium hydroxide content is lower in the case of L-type binders, which may suggest the binding of calcium from the intergranular solution in the form of other hydrocomposites by activating the slag in the composition, especially at longer curing periods;

The fact that the mass losses recorded between 60-215 ° C are higher for the cement-based binders L, which could suggest the formation of a higher amount of etringit beneficial for chromium inertization and a higher amount of calcium hydrosilicates gelici.

On the EDX spectra for samples based on cement containing waste, the presence of chromium is observed regardless of the curing period, which may suggest its immobilization in hidratated phases, in the form of insoluble salts, by substituting sulfate groups in ethingite (Cr-Et). , in accordance with FT-IR information, or by adsorption on hydrosilicates as indicated in the literature data [178,187-188].

Diffractometric analyzes performed on anhydrous binders revealed the following mineralogical phases: tricalcium silicate, dicalcium silicate), calcium ferritaluminate (brownmilerite), aluminattricalcium, gypsum. Also, the diffraction analysis performed on the dry waste at 50 ° C for 48 h, and then homogenized in a planetary ball mill for 30 minutes revealed as main crystalline phases calcium carbonate, calcium hydroxide and magnesium hydroxide. Thus, it was concluded that the waste used is basic, having an important content of calcium and magnesium. Chromium is also present, exceeding 2%.

Subsequent analyzes confirmed the presence of these constituents in the mass of the final materials obtained as well as the immobilization of chromium in the binders used without significant alteration of the mechanical properties of the mortars made.

The immobilization capacity of the waste in the studied binders was demonstrated by the results of the leaching tests performed. Thus, a good immobilization of chromium in the binder matrices was confirmed by the very low values of its concentration in the water that was in contact with the coded samples L and C.

In conclusion, it can be appreciated that the inertization of chromium in mortars, using the solidification / stabilization process is an efficient and safe solution for the elimination of hazardous waste from the potassium chromate manufacturing industry.

Also, according to the data found in the literature, it can be appreciated that the solidification / stabilization of toxic substances (with varying content of heavy metals, other than chromium), in binder matrices based on Portland cement, can be considered a means of disposing of hazardous waste. [221-223]

6.2 Inertization of chromium-rich waste into binders specially designed for the immobilization of harmful waste

Another objective of the thesis was the study on the inertization of a chromium-rich waste from the manufacture of potassium dichromate, in two types of Portland cements, which are designed for this purpose as part of the INERCEM range. At the same time, the influence of this waste on the hydration and hardening processes, as well as the properties of the resulting binders was followed.

The binder compositions obtained on the basis of the chromium-rich waste and of the two types of INERCEM are given in table 6.10, the waste being dosed so as to bring 0.5 and 1% chromium (% grav.).

The main properties investigated for binder systems were: water of standard consistency; setting time on pasta of normal consistency; mechanical strengths developed up to a period of 90 days on plastic mortar samples; immobilization of chromium in binder matrices.

It was observed that the increase in the waste content leads to a decrease in the value of water of standard consistency for both types of binders, in correlation with their specific surface values.

A significant increase in temperature (above 50 ° C) was also observed during the mixing of D0 cement with water; this exothermic process is mainly due to the presence of lime in the cement formula D. This could also explain the increase in the amount of water of standard consistency for this category of binders.

The presence of waste leads to a delay in the initial setting time compared to the waste-free binders - C0 and D0, but the final setting time varies insignificantly for cement type C, but more importantly for cement type D. These results are in accordance with the literature specialized, which explained the delay of the hydration process of the cement by the formation of chromium salts with low solubility on the surface of the binder particles and the adsorption of chromium ion on the calcium hydrosilicate gel (CSH) [225].

Type D binders, with / without waste content, regardless of the curing period, lack mechanical strength, most likely due to the tensioning of the curing structure through a very high interaction speed (correlated with the high heat value). hydration recorded in these systems). For mortars based on type C binders (without and with waste content), the values of compressive strength generally increase in up to 28 days; after this period, very small variations in mechanical strength can be explained by the carbonation process.

The presence of waste with a high chromium content in the binder mixture inhibits the hydration process of the cement and therefore inhibits the formation of hydrocomposites, including calcium hydroxide, which is highlighted by X-ray diffraction, with a decrease in the intensity of specific interferences. of them; at 90 days, this decrease can also be explained by the carbonation of hydrocompounds.

As can be seen, etringite is formed starting from 3 days of hydration, and its evolution over time is discontinuous, due to its partial transformation into the monosulfate compound (Afm). Monosulfate (AFm) is detected by very low intensity lines, which makes it difficult to detect X-ray (in 90-day hardened C0 paste it is observed that the lines characteristic of etringite disappear, and the characteristic lines of monosulfate do not appear).

Considering the information from the literature [211, 214] it can be assumed a low degree of crystallinity of this phase, due to its incorporation or intercalation in the mass of calcium hydrosilicates, poorly crystallized.

Also, in cement pastes with added waste, the formation of etringit seems to be favored, its interferences being more intense than in the paste without waste. The same variation / influence is manifested by the presence of slag in the binder (comparison C to D).

The following conclusions could be drawn from the study:

• the presence of waste in the case of type D binders can lead to significant alteration of the mechanical properties of mortars compared to type C binders;

• chromium can be immobilized in these binder matrices, but only for low concentrations (maximum 0.5% chromium in the hardened binder mass);

• at high concentrations of waste in the binder mass, the weak immobilization of chromium was confirmed by the relatively high values of its concentration in the water that was in contact with the coded samples C and D.

Chapter 7. Sludge / leachate from a landfill inertization in different types of binder mixtures

7.1 Leachate inertization into special binders designed for the immobilization of harmful waste

Therefore, another objective of the thesis was to provide solutions to the problem of wastewater (leachate) from municipal landfills, which cause serious damage to the environment by infesting the groundwater.

The aim was to demonstrate from a technological, chemical and commercial point of view that some wastes, such as light and heavy ash, from thermal power plants, blast furnace slag, or other by-products from cement plants (eg cement powder) can be used. pass) and special cements (eg INERCEMURI) for solving the leachate problem from such deposits. This solution can be implemented at any of the municipal landfills in the country.

In order to achieve this goal and to demonstrate the practical opportunity of this technical solution, several mixtures with the above materials were prepared and tested in the laboratory, in different proportions, constituting the binder inertization matrix, taking into account economic, with wastewater from municipal landfills. These mixtures were tested in the laboratory at predetermined curing intervals between 0-60 days (0, 3, 7, 14, 28 and 60 days) to determine:

- which composition ensures the best immobilization of harmful elements;
- which is the mixture for which the amount of wastewater incorporated is maximum;

which of the mixtures develops, over time, acceptable mechanical strength.

The analysis of the hardened pastes showed that the resulting binder matrices are stable in terms of chemical composition, obtaining materials with a very good inertization capacity.

The analysis of the chemical composition of the materials used showed that the heavy ash E has a content of 19% CaO, while the light ash T only 7%; at the same time, in terms of SiO2 content, it was much higher in light ash T. These compositional characteristics were also reflected in the setting times, which were shorter in the case of binders based on heavy ash E which proved to be be more basic.

The X-ray diffraction analysis showed that type T ash is a material with a lower degree of crystallinity compared to type E ash and therefore more reactive with respect to Ca (OH) 2 in the intergranular fluid of the binder system, and the sewage sludge has a high content of sodium and potassium salts mainly.

Cast binders have developed mechanical strength, even if their value is modest.

Scanning electron microscopy images are closely related to diffractograms and derivatograms of hardened binders, highlighting the presence of etringite crystals (prismatic, acicular morphology crystals), calcium hydrosilicates (very fine acicular crystals), but also carbon phases. (of undefined morphology). Even on the surface of the ash granules (spherical in shape) the presence of these curing phases is observed, which may suggest that their reactivity is high. On the leachate, heavy metal analyzes were performed and a good inertization of the heavy metals was shown in these studied binder matrices.

Although initially all components of the studied binder system (ash, inertia and leachate / sludge) were contaminated with heavy metals, leachate tests for binder masses in the form of hardened paste 28 days in powder form confirmed to us that in following the hydration-hydrolysis processes, the heavy metals were retained in these binder matrices, forming compounds with a very low water solubility. Virtually all leachate had quantities of heavy metals well below the legal limit legally imposed by Order 95.

This good retention of heavy metals can be explained by the high capacity of etringite to retain heavy elements in its structure, as well as their adsorption capacity on the surface of hydrosilicates

CONCLUSIONS

C.1. General conclusions

The objective of this paper was to *study the possibility of inertization and immobilizing some waste in inorganic binder matrices based on Portland cement, as well as studying their influence on hydration-hydrolysis processes and the properties of mortars based on these cements*.

The hydration process of the mineralogical phases in cement has been intensively studied, and it can be stated that the hydration of cement takes place in three consecutive stages: hydrolysis of mineralogical phases, precipitation of CSH, portlandite and other reaction products, respectively achieving a state of equilibrium between hydration.

Heavy metals usually modify these hydration reactions in the sense that they can influence the formation of hydration products of the binder system as well as their properties by altering the nucleation processes and increasing the reaction products.

Heavy metal inertization technology through the S / S process is a useful and efficient method of waste management in avoiding the contamination of the environment with metallic pollutants from various branches of industry. The effectiveness of this method can be improved by modifying the phases of mortars / concretes and controlling parameters such as temperature, water: solid ratio, particle size, etc., so as to achieve the desired mechanical properties while inhibiting harmful actions that are characteristic of heavy metals.

Another problem that arises when we talk about the inertization of heavy metals in inorganic binder matrices, is that the phases associated with heavy metals immobilized in mortar / concrete matrices often have an amorphous or weakly crystalline structure which can make the process of characterization of the obtained materials very difficult. Due to this, there are some contradictions regarding the main mechanism for fixing various metals in the structure of mortars / concretes. Thus, it can be concluded that there may be several ways of inertization heavy metals in inorganic binder matrices.

Cement stone seems to be an ideal material for inertization harmful substances, both in terms of the efficiency of the asset and in terms of costs involved. Given its relatively high compactness, it acts both as a physical barrier to solubilization and leaching of harmful substances, and as a participant in the reaction, with the formation of sparingly soluble compounds, stable in the basic pH environment, specific to cement stone.

At lower concentrations of harmful substances, their fixation in cement stone is done preferentially by adsorption - mainly on the surface of the hydrosilicate phases, as well as by the formation of solid solutions with certain crystalline hydrocomposites. At higher concentrations, the fixation of harmful substances takes place mainly by the formation and precipitation of hardly soluble, stable compounds. By such types of reactions can be immobilized in stable compounds, including amphoteric elements, whose solubility at basic pH is high.

The ability to fix harmful substances increases with the duration of hydration of the cement. As hydration progresses, the porosity of the cement stone decreases, so the physical barrier to the penetration of a leachate becomes more efficient. In addition, the processes of interaction between harmful substances and the cement stone progress, with the formation of hardly soluble compounds.

The stability of the binder matrix and implicitly the efficiency of the inertization are strongly influenced by the characteristics of the leaching agent, with which it comes into contact. In contact with a neutral leaching agent, such as plain water, after a short time the cement stone imprints a basic pH on it and an equilibrium situation is reached. If the cement stone comes in contact with a leachate kept constantly at a neutral pH (eg running water) or even acid, its stability is severely affected and the ability to immobilize harmful substances is lost over time. These considerations *must* be taken into account in the judicious choice of solubilization and leaching tests and in assessing the usefulness of the results thus obtained, for the long-term prediction of the ability to immobilize harmful substances in the cement stone.

C.2. Original contributions

In the present doctoral thesis, waste was used as a constituent part of all binder mixtures that were studied. Limits and limitations on their use in these mixtures could be highlighted. Therefore, the following were shown:

❖ ***wastes or by-products from different industries other than inorganic binders can be used as additives in different stages of obtaining these binders***, as follows:

➢ when using a heavy ash resulting from the energy industry (burning coal in a thermal power plant) as a secondary raw material, precisely as a ***corrective addition*** to the mixture of raw materials. Its presence did not significantly change the chemical-mineralogical characteristics of clinker obtained by; therefore, it did not change the hardening behavior nor the physical-mechanical characteristics after hardening of the binder system;

➢ when replacing the clinker with a light ash from a different source, from the energy industry (most often used), actually from the manufacture of the chip, in ***addition to grinding*** it, to obtain Portland cement, mixed binders with characteristic binding properties that it is possible to use them in practice.

➢ Hydration-hydrolysis processes have also been found to be slowed down by the increase in ash content due to cement dilution, and the nature of the hydration phases is similar to that of hydrated unit Portland cement. It has been shown from determinations that for a degree of substitution of 10% of Portland cement with ash, an optimal mechanical behavior is obtained;

❖ ***wastes or by-products from different industries can be inerted in different binder matrices***, as follows:

➢ the influence of the use as addition in the lined matrix of a waste rich in chromium, coming from the industry of obtaining potassium dichromate was analyzed, being considered two cases:

- its inertization in ordinary binder matrices, based on Portland cement, type II cements A - M and A - L;
- its inertization in special binder matrices, based on Portland cement, type II cements B-M, called INERCEM C and D.

The following were found:

➢ in the ordinary Portland cement-based binder matrices in terms of mechanical strengths, a better behavior was observed for the binder masses with and without the addition of L-type cement waste, compared to the cement-type binder mixtures M, which were slightly weaker. Over time, the behavior of these binder matrices was similar.

- also, the systematic decrease of the mechanical resistances was identified with the increase of the weight of waste in the mixture, which was attributed to the dilution of the cement in the binder mass;
- in the binder matrices based on special cements INERCEM C and D, from the point of view of mechanical strengths, it was observed that only binder mixtures without and with waste based on INERCEM C developed some mechanical strengths. The binder masses without and with waste based on INERCEM D did not develop mechanical strengths during the studied curing period.
- it has also been observed that mechanical strength decreases with increasing weight of the mixture, which is explained by the dilution of cement in these masses or the slowing down of the hydration process of cement by the presence of waste and therefore the formation of hydrocomposites, including calcium hydroxide.
- from the point of view of inertization the harmful elements in ordinary Portland cement-based binders, although the concentration of chromium in the leachate has increased in proportion to the amount of waste added, however, it has not exceeded the limits imposed by Regulation 95, up to a weight of 36.9% mass percentage of waste in the binder matrix, either type M or type L, chromium inertization is done successfully;
- from the point of view of inerting the harmful elements, in binder matrices based on special cements INERCEM C and D, the concentration of chromium in leachate increased proportionally with the amount of waste added, however, did not exceed the limits imposed by norm 95 to a weight of waste in the binder matrix of 18.45% mass percentage. Above this limit, in the test performed for a weight of 36.9% mass percentage of waste in the binder matrix, both matrices revealed a concentration of approximately 200 mg / kg for chromium present in the washing water, which far exceeds 70 mg / kg imposed as the maximum limit allowed by order 95;

- ***leachate / sludge from a landfill can be inerted in different binder matrices***, as follows:
  - This study was based on the requirement of ORDER No. 757 of November 26, 2004 on the inertization of waste in binder matrices based on Portland cement.
  - In this case, mixed binders based on IERCEMs A and E were used mixed with two types of ash - heavy (E) and light (T). It has been shown that they can be used successfully for the disposal and embedding of leachate from municipal landfills. Reinforced binders, due

to their high ability to immobilize and inertize harmful elements, can be used, for example, to close(plug) that pit.

C.3. Prospects for further development

All the studied cases can be replicated at pilot level, they being important results that are solutions worth following to ensure the good inertization of this type of waste. Taking into account both economic and environmental implications, it can be estimated that these waste inertization and immobilization solutions can be applied at the macroeconomic level.

Results dissemination

Papers published in ISI listed journals (F.I. cumulat = 6,039)

1. **C. L. Oproiu**, G. Voicu, A. I. Nicoară, A. I. Bădănoiu, "The Influence of Partial Substitution of Raw Materials with Heavy Ash on the Main Properties of Portland Cements", Journal of Chemistry, Bucharest, Vol, 69, no, 4, 2018, 860-863
2. **C. L. Oproiu**, M. Pârvan, G. Voicu, AI Bădănoiu, "Inertization of an industrial waste rich in chromium in portland composite cements", Romanian Journal of Materials, 2018, 48 (4), 458-466
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3. **C.Oproiu**, G. Voicu, A.-I. Nicoară, A.-I. Bădănoiu, "Binding properties of masses based on clinker obtained by using fly ash as one component of raw materials", S6-125, 20th Romanian International Conference on Chemistry and Chemical Engineering (RICCCE 20), September 6-7, 2017, Brasov, Romania.