A THERMAL ANALYSIS STUDY ON PROPRIETARY QUICK-SETTING MIXED BINDER SYSTEM

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ABSTRACT

The present paper presents a study, by thermal analysis, of the hydration of a mixed binder system consist of Portland composite cement type CEM II/A-M(S-LL) 32,5 R and calcium aluminate cement type GORKAL 70, patented by the authors for embedding spent radioactive solvents. Cement hydration reactions are often affected by the presence of a spent radioactive solvent, usually retarded. This process can be monitored by thermal analysis and often quantified. The data are being used as a reference to compare the changes in the cement blend hydration during the solidification caused by the presence of the spent radioactive solvents itself or by emulsifier additives which are being availed. Detailed analysis of DTG (derivative thermo gravimetric) decomposition profiles of portlandite and carbonate enabled the evaluation of admixture-related parameters concerning portlandite formation and also indicated the behaviour of specific carbonates during the hydration process.

Key words: (Portland cement blended, calcium aluminate cements, spent radioactive solvents, thermal and thermo gravimetric analysis)

Introduction

The purpose of our research was the investigation of the effects of various solvent on 28-day hydration of a mixed binder system consist of Portland composite cement type CEM II/A-M(S-LL) 32,5 R and calcium aluminate cement type Gorkal 70. The composition of hydrated cement paste was evaluated by thermogravimetric/derivative thermogravimetric analysis (TG/DTG) which has had a long tradition in studies on hydrated cements.

Scientific literature contains an ample amount of papers dealing with the applications of thermal analysis (TG/DTG-DTA or DSC) to broad aspects of the Portland composite cement and calcium aluminate cement hydration process and its chemistry although most studies are necessarily specifically oriented to coincide with the purpose of a particular research topic During the hydration of Portland cement clinker minerals react with water yielding a complex microstructure consisting mainly of amorphous calcium silicate hydrate gel ($1.7CaO \cdot SiO_2 \cdot 1.5H_2O$; C-S-H in cement chemistry notation), ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), portlandite ($Ca(OH)_2$), carbonated phases and calcite ($CaCO_3$). When blast

furnace slag and limestone are present in Portland cement, the rate and degree of hydration change, as does the composition of the hydrated cement paste.
Several Differential Thermo Gravimetric (DTG) curves of calcium aluminate cement are published in the literature. Compared to systems based on portland cement, calcium aluminate cement remains a relatively little studied material in the field of cement and concrete science. Several works have been carried out during the past few decades to understand the mechanisms of calcium aluminate cement hydration and the conversion of the related hydrates. Calcium alumina cement a type or amongst non Portland cements. An increase in the use of this cement was observed in the past by combining with other binders (Portland cement, granulated blast furnace slag, fly ash) and usually serves as a binder mixture for different applications [1-14].
There are a variety of matrix materials and commercially techniques available for conditioning organic radioactive wastes [15-17]. The papers [18, 19] provide an overview of the application context and evolution of several important matrix materials and offers comments on the waste form requirements under disposal conditions. In this paper emphasis has been placed on the conditioning options available commercially and that have, to various degrees, been demonstrated to be viable. At the same time, it is recognized that other matrices are being researched as possible for future options. Included in these options are magnesium phosphates binding systems [20] and mixed cement with Portland composite cement and Calcium Aluminate Cement [21]. In recent years, studies were undertaken on the possibilities to use mixed cement with Portland composite cement and Calcium Aluminate Cement from for conditioning organic radioactive wastes [22].
The hydration processes can be identified and explained using any analytical tool. In previous studies [23] calorimetry was used to determine the properties of the paste of the mixture of Portland cement with calcium alumina cement with various amounts of different types of solvent (methyl alcohol and toluene) and emulsifier additives. Thus effect has been shown to delay the different types of solvent on the well-known matrix accelerated conditioning outlets using scanning electron microscopy and determination of heat of hydration.
A mixed binder system consist of Portland composite cement type CEM II/A-M(S-LL) 32,5 R and calcium aluminate cement type GORKAL 70, are patented [24]. The invention relates to a process for embedding mixtures of tritium-contaminated spent radioactive solvents into quick-setting mixed binder systems and to a matrix for conditioning such radioactive organic wastes. At SCN Pitesti and ICECHIM Bucharest where the main experimental work is carried out on the selecting the best additives from replace the nonylphenol ethoxylates used from emulsified the organic liquid radioactive wastes. It was proved that the emulsifier aditives type polyoxyethylene alkyl(C_{12-14}) ethers patented [25] for conditioning radioactive oils and solvent could meet the Waste Acceptance Criteria of the waste form the disposal site and Romanian legislative framework harmonized with international legislation [26].
In the present study it has been planned to explain the hydration process through TG/DTA. The results presented in this work concern avoidance of conversion of aluminates and possibilities of usage of the binders for conditioning of the radioactive solvent organic wastes resulted from nuclear power plant decontamination operations.

Materials and methods

The aim of this work was investigation of hydration of blend calcium aluminate cement and portland compozite cement in the presence of emulsification additives and VARSOL (white spirite).
The following materials were used in the study:
- High aluminate cement of grade Gorkal-70 produced by the Gorka company (Poland). Its chemical composition is (%): Al_2O_3 70.2, Fe_2O_3 up to 0.12, CaO 28.0. The main minerals are CA ($CaO{\cdot}Al_2O_3$) and CA_2($CaO{\cdot}2Al_2O_3$).

- Portland composite cement type CEM II/A-M(S-LL) 32,5 R produced by the Holcim company (Romania). Constituents (in accordance with SR EN 197-1:2002) are (%): Portland clinker 80 – 94, additives (blast furnace slag and limestone), 6 - 20 and anhydrite as retarder.
- solvent type Varsol is the ExxonMobil Chemical brand for a line of conventional aliphatic fluids boiling in the mineral spirit or white spirits range.
- distilled water
- emulsifier additives type FINDET 1214N/15 (Polyoxyethylene(3) alkyl(C_{12-14}) ethers) and FINDET 1214N/21 (Polyoxyethylene(9) alkyl(C12-14) ethersrespectively, produced by the Kao Corporation S.A.

Cement pastes made with water/binder ratio = 0.27 to 0.35 were studied. Solvent type Varsol was introduced as 17,5%. Samples denoted as 1-5 (**Table 1**) were stored in hermetic plastic bags in the temperature of 18–20^{0}C. On a 28 day of hydration pastes were removed from the bags, ground and studied using TG/DTG method.

Table 1 *Composition of cement pastes*

SAMPLE	CEM IIA/M [%]	GORKAL [%]	WATER [%]	VARSOL [%]	FINDET [%]	Water to binder ratio
1	75.2	0	24.8	0	0	0.33
2	0	75.2	24.8	0	0	0.33
3	65.3	9.9	24.8	0	0	0.33
4	65.3	8.9	24.8	0	1.0	0.33
5	55.3	8.7	17.5	17.5	1.0	0.27

The following experimental equipment was used SHIMADZU DTG-60/60H. Simultaneous Thermogravimetry/Differential Thermal Analyzers, sample mass cca. 30 mg, temperature increase rate of 10^0 C/min, as the purge gas 100 ml/ min of air and 30 cm^3/min of nitrogen, respectively.

Results and discussion

Figures 1-4 presents the comparison of DTG curves obtained for sample 1-5 pastes after 28 days of hydration.

The DTA curves (**Figure 1**) of cement CEM II A/M (sample 1) is distinguished three groups of transformations, in the following way:

- the peaks at 108°C, 171°C are due to the physically sorbet water dehydration of C-S-H gel
- the peaks at 182°C, 362°C are due to decomposition of a complex mixture of hydrated silicate- and aluminate-type compounds;
- the peak at 444 °C is due to the decomposition of the portlandite $Ca(OH)_2$ from the binder;
- the peak at 744 °C is due to decomposition of carbonated phases and calcite $CaCO_3$. Under normal conditions of hydration it is difficult to prevent some carbonation of lime that is formed. At higher temperatures some peaks may occur due to crystalline transformations.

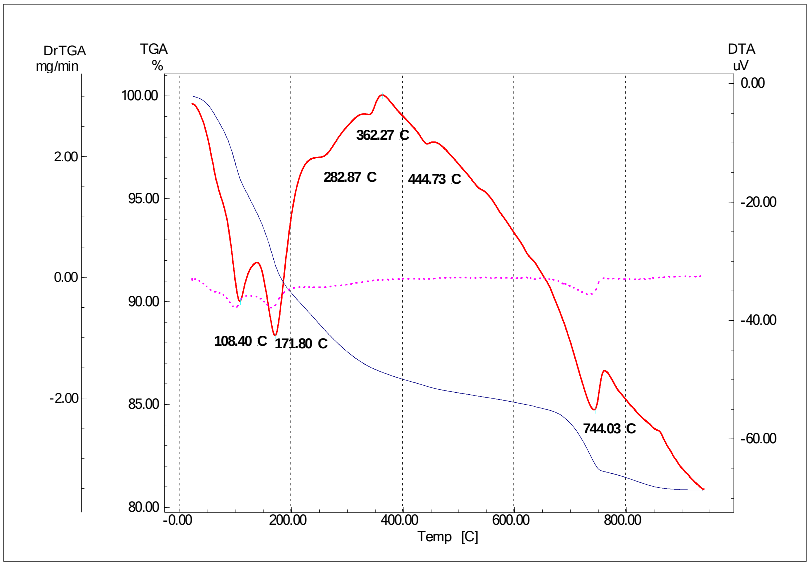

Figure 1 *DTA,TG and DTG curves of Portland composite cement type CEM II/A-M(S-LL) paste*

For sample 2 (**Figure 2**) the characteristic effects can be observed which can be interpreted in the following way:

- peak maximum at 126,7^0 C – dehydration of AH_3 gel and CAH_{10} phase;
- at 295,1^0 C – dehydration of C_2AH_8 and dehydration of AH_3 (gibbsite) and probably dehydration of C_3AH_6;
- a very small scale peak at 674,2 probably decomposition of carbonate phases (Calcium hemicarboaluminate phases/ Calcium monocarboaluminate phases).

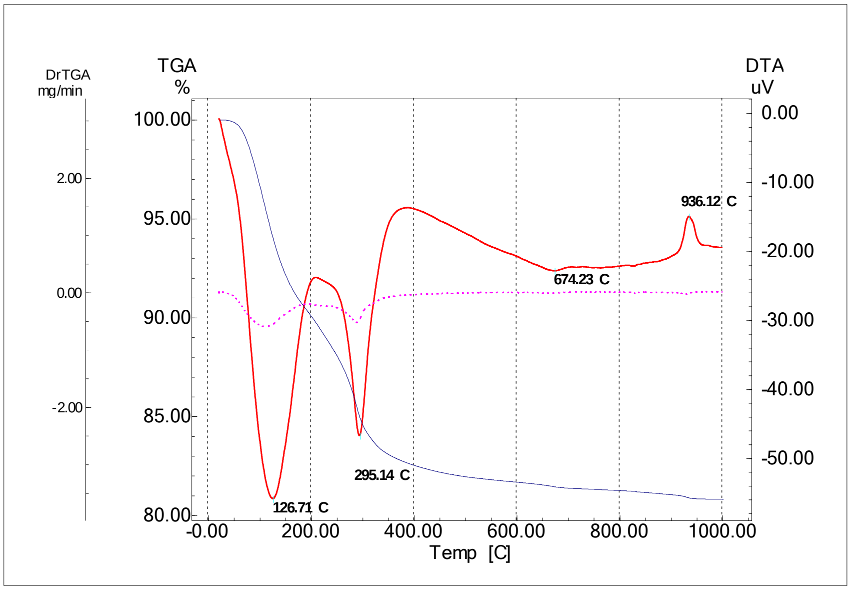

Figure 2 *DTA,TG and DTG curves of calcium aluminium cement paste*

Figure 3 and **4** show the DTA,TG and DTG curves of the mixed Portland composite cement type CEM II/A-M(S-LL) 32,5 R and calcium aluminate cement type Gorkal 70 pastes (sample 3) *mixed Portland composite cement type CEM II/A-M(S-LL) 32,5 R, calcium aluminate cement type Gorkal 70,FINDET and VARSOL (sample 5)* and after 28 days of hydration. The DTG curves of sample 3 (**Figure 3**) is distinguished four groups of transformations, in the following way:

- the peaks at 74°C, 108°C, 171°C are due to the physically sorbed water dehydration of C-S-H gel
- the peaks at 266°C, 332°C are due to decomposition of a complex mixture of hydrated silicate- and aluminate-type compounds;
- the peak at 440 °C is due to the to decomposition of the portlandite $Ca(OH)_2$ from the binder;
- the peak at 737 °C is due to decomposition of carbonated phases and calcite $CaCO_3$. Under normal conditions of hydration it is difficult to prevent some carbonation of lime that is formed. At higher temperatures some peaks may occur due to crystalline transformations.

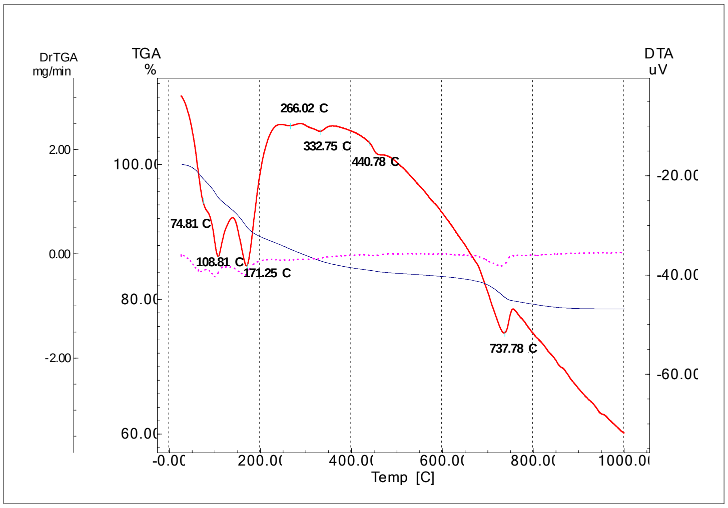

Figure 3 *DTA,TG and DTG curves of mixed Portland composite cement type CEM II/A-M(S-LL) 32,5 R and calcium aluminate cement type Gorkal 70 paste*

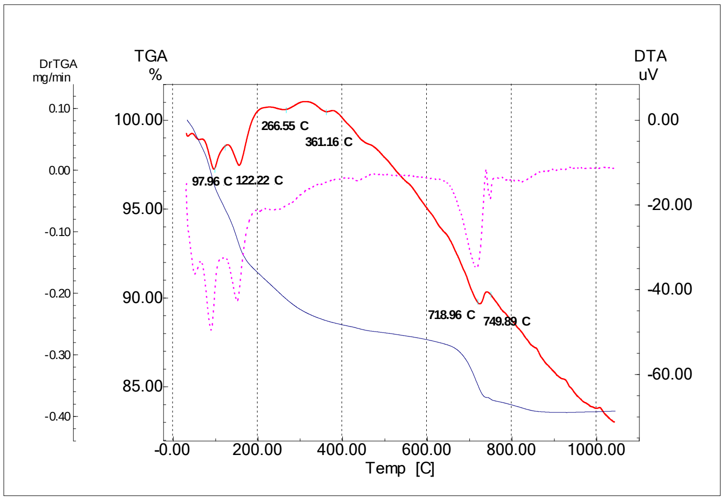

Figure 4 *DTA,TG and DTG curves of mixed Portland composite cement type CEM II/A-M(S-LL) 32,5 R, calcium aluminate cement type Gorkal 70,FINDET and VARSOL paste*

TG/DTG thermal analysis allows estimation of sample composition basing on characteristic effects of mass losses. The products of hydration and carbonation of cement dehydrate and decompose in different temperature ranges. Studied system is multicomponent and the effects of dehydration of different products can occur often at similar temperatures. The Weight loss measured by TG and DTG of sample 1-5 is represented in **Figure 5**.

From the results it was found that TG between 30-200^{0}C most samples exhibited the highest mass loss attributed to the presence of aluminate hydrocarbon phases. The second range of temperatures between 200-400^{0}C, attributed to the presence C_3AH_6 and AH_3, weight loss is around 4% is for the controls, with / without additive emulsifier, respectively containing VARSOL, with the exception of the calcium aluminate cement pastes (7,3%). The loss of mass attributed to remove water or Ca(OH)2, in the second range of temperatures (400-600^{0}C), is around 3% from Portland composite cement paste and less to 1% for mixed Portland composite cement type CEM II/A-M(S-LL) 32,5 R, calcium aluminate cement type Gorkal 70,FINDET and VARSOL pastes. In the temperature range 600 to 1000^{0}C, assigned to $CaCO_3$ decomposition coming from Portland cement composite (more crystalline), the Weight losses is less than 0.5% for the controls and around 4 % of the sample embedded the emulsifier additives (FINDET) and the solvent (VARSOL).

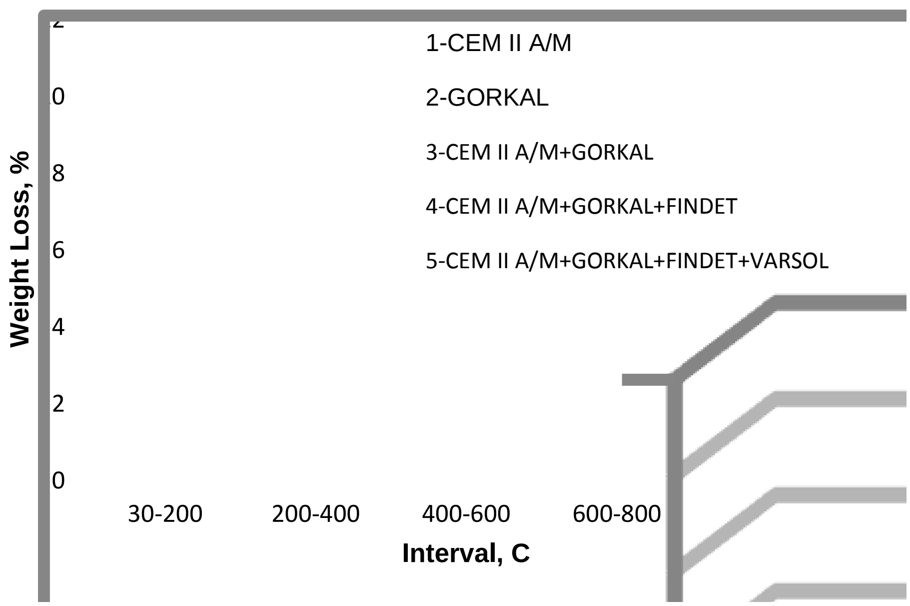

Figure 5 *Weight losses measured by TG and DTG of sample 1-5*

Conclusions

The presence of solvent VARSOL influences mixed cement hydration.

This work has met the objective of providing, by thermal analysis characterization, a reference database of the hydration of the Portland cement blended with calcium aluminium cement, which is being used to solidify liquid radioactive wastes.

Glossary/notation

A simplified notation is used when describing cement compounds, the cement shorthand notation: C = CaO, S = SiO_2,H = H_2O, A = Al_2O_3,F = Fe_2O_3,CC = CO_3.
This leads to the following abbreviations for anhydrous and hydrates phases:
CA_2($CaO·2Al_2O_3$), C_3A (3CaO. Al_2O_3) -Tricalcium aluminate
CSH (CaO. SiO_2. H_2O) - Calcium silicate hydrate
CASH (CaO. Al_2O_3. SiO_2. H_2O) - Calcium silicate aluminate hydrate
CAH_{10} (CaO. Al_2O_3.10 H_2O) - Calcium aluminate deca hydrate
AH_3 –gibbsite gel
CC ($CaCO_3$) - Calcium carbonate, calcite
CH ($Ca(OH)_2$) - Calcium hydroxide, portlandite
C_2AH_8 (2CaO. Al_2O_3.8 H_2O) - Calcium aluminate hydrate
C_2ASH_8 (2CaO. Al_2O_3 SiO_2.8 H_2O) - Calcium silicate aluminate hydrate
C_3AH_6 (3CaO. Al_2O_3.6 H_2O) - Calcium aluminate hydrate
3CaO.Al_2O_3. 0.5$Ca(OH)_2$. 0.5 $CaCO_3$. 11.5H_2O - Calcium hemicarboaluminate phases 3CaO. Al_2O_3. $CaCO_3$. 11H_2O - Calcium monocarboaluminate phases
The following abbreviations are also used:
DTA -Differential Thermal Analysis
TGA -Thermogravimetric Analysis
FINDET- emulsifier aditiv
GORKAL- calcium aluminat cement

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