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SUMMARY OF THE DOCTORAL THESIS

CONTRIBUTIONS TO THE ASSESSMENT OF THE DURABILITY OF ENGINEERED BARRIERS WITHIN A RADIOACTIVE WASTE REPOSITORY

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MOTIVATION

The choice of this topic is motivated by the need to deepen and improve the understanding of the long-term behavior of engineered barriers, especially under complex stress conditions such as those found in the host environment of a radioactive waste repository: water infiltration, chemical interaction with degradation products, or structural changes over time. Assessing the durability of these structures is a critical step in ensuring their functionality over long and very long periods of time.

At the same time, the national and European context related to the scheduled closure of nuclear reactors, respectively the construction of waste repositories, makes the subject both timely and of strategic interest.

Moreover, one of the observations made by expert missions requested by the Nuclear and Radioactive Waste Agency and the National Commission for Nuclear Activities Control, during the analysis of the preliminary safety documentation for the future radioactive waste repository, was the need to implement a research program to demonstrate the durability of cement-based materials used as engineered barriers (waste conditioning matrix, construction material for modules and disposal cells). For this reason, the Nuclear and Radioactive Waste Agency, based on a collaboration protocol with the State Owned Company Technologies for Nuclear Energy – the subsidiary the Institute for Nuclear Research Pitesti, requested the inclusion in the research program of a dedicated topic aimed at understanding the behavior of cement-based materials and demonstrating their durability over periods of approximately 300 years under the specific conditions of Saligny site.

In this context, the choice of the topic ***Contributions to the Assessment of the Durability of Engineered Barriers in a Radioactive Waste Repository***, with a focus on evaluating the durability of cement-based engineered barriers, becomes a pressing necessity for anticipating how these structures behave and degrade on the long run. It also supports the optimization of design and material composition, as well as compliance with the strict requirements of national and international regulations regarding operational safety and nuclear security, and the protection of the population and the environment.

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1 INTRODUCTION

This chapter presents aspects related to the importance of the safe management of radioactive waste, the unwanted but inevitable part of using ionizing radiation—a type of management that represents a major long-term challenge for the nuclear industry and for environment protection.

The necessity of containing and isolating this type of waste from humans and the environment is addressed through the implementation of appropriate storage systems that employ a multibarrier approach, consisting of a sequence of natural and engineered barriers, with particular emphasis on the system of engineered barriers.

The importance of understanding the behavior and evolution of the properties—and consequently the durability—of the materials used in these systems is also addressed, with a focus on cement-based materials. This emphasis is justified by the estimation that a very high proportion (over 90%) of the constituent materials in the engineered barriers of near-surface disposal systems are composed of this type of material.

At the same time, the fundamental role of using modeling with dedicated software (PHREEQC, GEMS, etc.) is also mentioned, with the help of which the evolution of these materials can be estimated over a very long period of time, compared to experimental studies that can be carried out over limited periods of time.

2 THE CURRENT STATUS OF RESEARCH ON CHEMISTRY, HYDRATION, DEGRADATION AND TRANSPORT THROUGH CEMENT-BASED MATERIALS

Chapter 2 provides a broad and well-structured overview of the current research in the field of cementitious materials, with a focus on the fundamental hydration, degradation and transport processes that determine their behavior over time, especially in the context of their use for insulation, protection or storage applications (including for radioactive waste).

2.1 Hydration mechanism of Portland cement and stability of the resulting phases

This section describes the basic chemical reactions that occur between the components of Portland cement and water, leading to the formation of the main hydrated phases: calcium hydrosilicate (C-S-H), Portlandite ($\text{Ca}(\text{OH})_2$) and other secondary compounds such as calcium aluminum silicate hydrate (C-A-S-H), ettringite, etc. [1] [2] [3].

It is highlighted the reaction behavior of each clinker phase and the corresponding hydration products it generates, along with the stability of these hydration products.

2.1.1 Modeling cement hydration processes

This section focuses on modeling methods that allow understanding and prediction of the hydration process using the two approaches mentioned by Šrāček et al [4] for the case of geochemical investigations, such as: **the thermodynamic approach** and **the kinetic approach**.

Thermodynamic modeling is presented as an essential tool for predicting the composition of solid phases and pore solution in chemical equilibrium. It is emphasized the importance of using databases (e.g. CEMDATA) and computer codes such as GEMS [5] and PHREEQC [6].

Unlike the thermodynamic approach, kinetic modeling introduces the time factor into the equation, thus allowing the analysis of the dynamics of the dissolution and hydration reactions of the cement phases over time. The Parrot and Kiloh models, well-known and used in many studies addressing this topic, are presented [2] [7] [8] [9] [10] [11] [12] [13] [14]. These models describe hydration as a diffusion-controlled process, where the diffusion coefficient is imposed by the slowest hydration rate of the clinker phase at time t .

2.2 Processes that can affect the durability of cement-based materials

This section deals with the main degradation mechanisms (leaching, carbonation, sulfate attack, and decalcification) that may compromise the durability of cement-based materials over time, especially in chemically aggressive environments.

It is described the mechanism by which these processes impact hydration products, especially $\text{Ca}(\text{OH})_2$ and C-S-H, such as their dissolution and migration out of the structure, ultimately resulting in loss of cohesion, alterations in porosity and permeability, and a reduction in mechanical strength.

The properties on which the extent of these processes depends are analyzed, as well as the reactions involved and the resulting products. Additionally, the impact of these products on the structure and chemical composition of the materials is also presented.

2.3 Synthesis study on the transport properties of cement-based materials

In this part of the thesis, the transport properties (absorption, permeability, diffusion) that control the migration of fluids and chemical species through the porous network are analyzed.

The retention mechanisms and sorption capacity of contaminants on cement-based materials are examined, as well as methods for quantifying and presenting sorption capacity in the form of a distribution coefficient (K_d) or a de-distribution ratio (R_d).

Water permeability, an essential indicator of durability, is discussed, influenced by microstructure and degree of hydration.

Ionic diffusion is analyzed, with emphasis on the transport of reactive species through the structure of porous materials based on the concentration gradient, with emphasis on the application of Fick's laws for a porous medium.

2.4 Conclusions

The chapter dedicated to the current state of research on cement-based materials highlights the significant progress made in understanding the chemical and physical processes that determine the performance and durability of these materials, providing a solid foundation for engineering applications in the field of sustainable and high-performance constructions.

In the design stage of cement-based materials, understanding the formation and stability of hydration products allows for the optimal selection of cement type and additives, depending on the structural demands and environment conditions.

Thermodynamic and kinetic modeling of hydration processes is already integrated and successfully transposed into software models for simulating hydration processes and other processes specific to these types of materials.

Degradation processes (leaching, carbonation, sulfate attack) are critical in assessing the durability of structures exposed to aggressive environments.

The analysis of sorption processes and transport processes is essential in assessing the penetration time of aggressive agents and migration of radionuclides from waste with direct applications in the design of engineering barrier systems.

3 ANALYSES AND EXPERIMENTAL STUDIES ON THE CHEMISTRY AND HYDRATION OF MATERIALS BASED ON COMPOSITE CEMENT CEM II/B-M TYPE

Chapter 3 presents a synthesis of the study conducted on the chemical properties and hydration processes of materials based on commercial Portland composite cement CEM II/B-M type (S-LL) 42,5 R.

The main aspects addressed in the study and presented in this chapter, include:

- **The chemical characterization of the component materials:** it is presented the chemical and mineralogical composition of the CEM II/B-M (S-LL) 42,5 R cement.
- **The hydration mechanisms:** there are analyzed the main stages of the hydration process, the formation and evolution of hydration products, as well as the degree of hydration;
- **The evolution of physicochemical and mechanical properties over time:** there are presented the results of experimental studies on changes in microstructure and mechanical strength depending on the duration of the hydration process.
- **The influence of environmental parameters:** it is presented how the hydration temperature influences the dynamics of hydration reactions and the final properties of the material.

3.1 Oxide and mineralogical composition

This subsection describes the chemical and mineralogical composition, determined through analyses and mathematical modeling, of the CEM II/B-M(S-LL), 42.5R type cement used as raw material in the samples subjected to experimental testing.

The reason why materials based on this type of cement were studied is that it represents the main binder of the conditioning matrix currently used in Romania in the radioactive waste conditioning process and which could also be used for the construction of storage cells of the future short-lived low- and intermediate-level waste repository at Saligny.

3.2 Experimental determination of the degree of hydration

This subchapter presents the results of the experimental determination of the degree of hydration of cement pastes or mortars, obtained as a combined effect between the use and solution of mathematical equations and the data obtained from thermal analyses, an experimental method that can be used to estimate the degree of hydration by coupling two techniques: differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

Thus, the determination of the degree of hydration was carried out using two methods. The first method uses the equations proposed by Chu *et al.* [15] and Whang *et al.* [16] which for their solution require the amount of Portlandite, quantified based on the DTA/TGA diagrams, while the second method uses in the first instance the equation of Chu *et al.* [15] to determine the amount of chemically bound water in a fully hydrated sample, which is subsequently introduced into the equations proposed by Panea *et al* and Pang *et al* [17, 18] which use chemically bound water to estimate the degree of hydration of a cement paste.

Figure 3-1 graphically represents the kinetics of the degree of hydration of a 720-day-old sample, obtained by applying the two methods mentioned above.

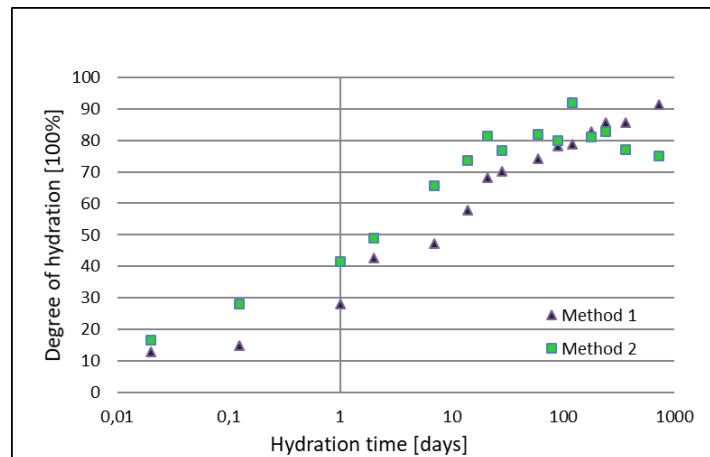


Figure 3-1. The hydration kinetics of a cement paste obtained by two different methods

From the analysis of the graph, it can be observed that the first method indicates that even after this period, hydration seems to continue, while the second method indicates that this process stopped, and even more so, it seems to be regressing, which cannot be real, and this is why the first method seems to reproduce better the hydration kinetics even more because there are phases in cement whose hydration is slower (such as C_2S).

At the same time, studies and calculations were carried out to determine the hydration kinetics of mortars. The previously described technique for determining the hydration kinetics of cement paste no longer seems to be so precise in quantifying Portlandite and implicitly in estimating the degree of hydration, since even if the introduced sand fraction is taken into account and the necessary calculations are made, there is no certainty that the analyzed sample is representative.

However, based on the TGA diagrams, determinations were carried out and led to the quantification of Portlandite and the estimation of the evolution of hydration kinetics, for both of which an upward evolution was observed as the hydration period increased.

3.3 The effect of temperature on the hydration process

This subchapter presents the effects of hydration temperature on the development of portlandite and implicitly on the degree of hydration, it being known that temperature is one of the determining external factors in influencing the normal process of dissolution of clinker phases and formation of hydration products [2] [7] [19] [20] [21] [22] [23] [24] [25] [26] [27].

For this purpose, thermal analyses were performed on cement pastes whose hydration took place at different temperatures (3, 22 and 38 °C). Figure 3-2 represents graphically the first-order derivatives (DTG) of the TGA diagrams. In this graphic representation it can be seen that significant processes took place; these mark the loss of physically bound water and hydration products such as CSH or Ettringite at temperatures below 100, dehydroxylation of Portlandite in the range of 400 ÷ 540°C, decomposition of CaCO₃ in the range of 600 ÷ 780°C.

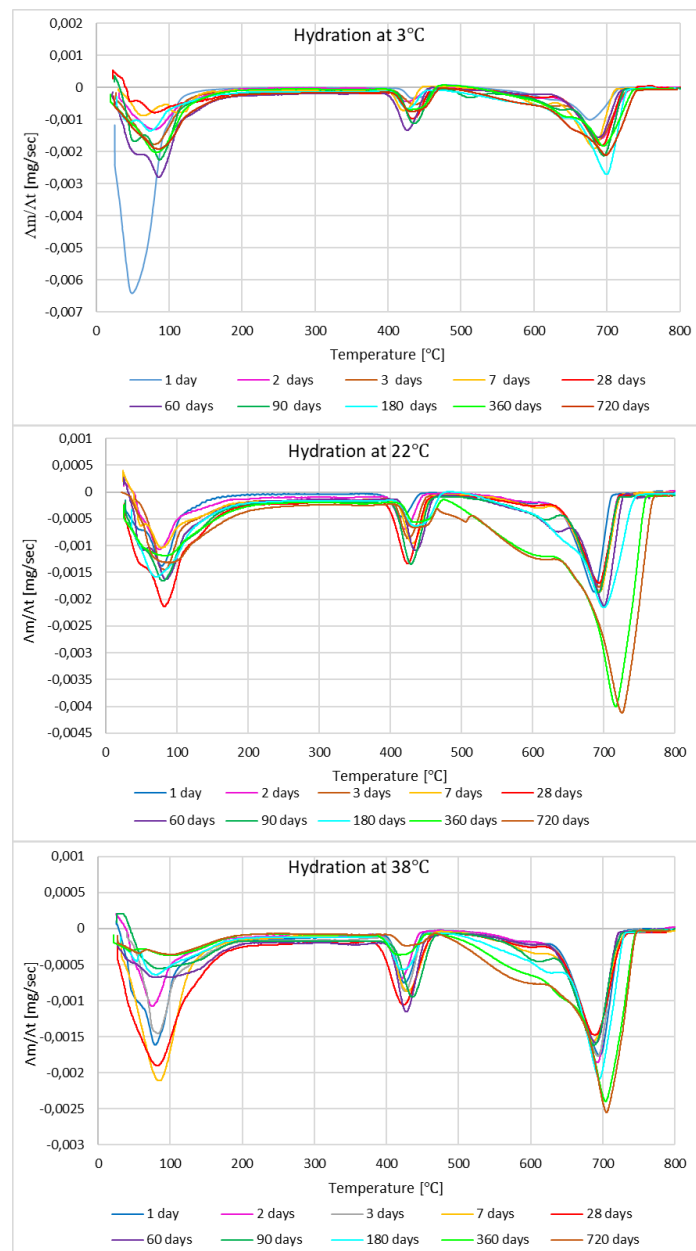


Figure 3-2. Graphical representation of first-order derivatives (DrTGA), obtained from analyses of hydrated cement paste samples for a period of 720 days

The hydration kinetics for the three temperature ranges are graphically represented in Figure 3-3 where a direct proportional relationship between the degree of hydration and temperature can be observed. This was expected, since Ca(OH)_2 , the element on the basis of which the degree of hydration is determined, is in the same dependence relationship with the hydration temperature (see Figure 3-4).

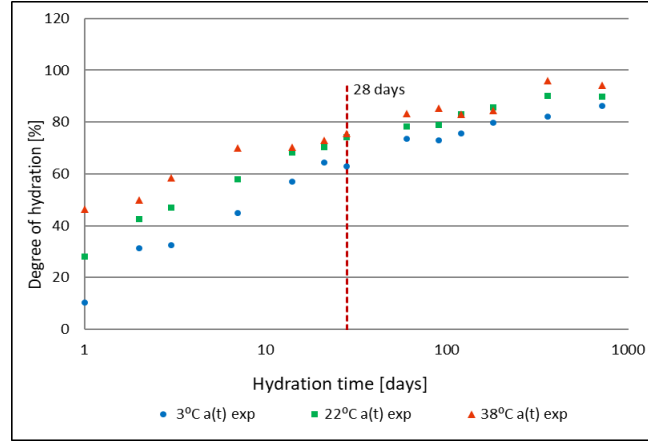


Figure 3-3. The effect of temperature on the degree of hydration

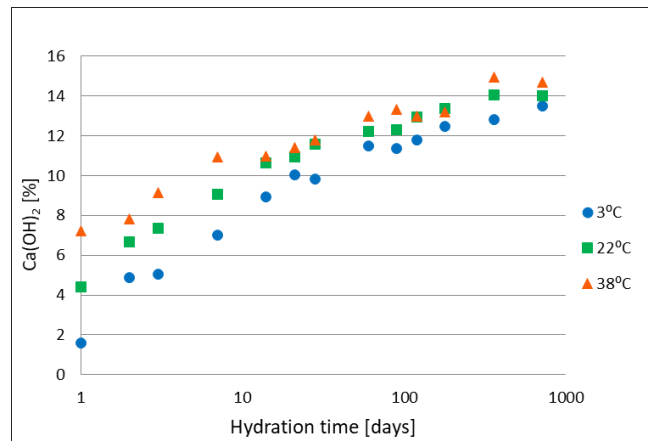


Figure 3-4. The effect of temperature on the development and evolution of Portlandite

Both in the quantification of Portlandite and in the determination of the degree of hydration, the same sequence of operations was followed, as previously presented, with the clarification that in the determination of the degree of hydration, it was used only the method based on the quantification of Portlandite based on TGA diagrams.

The comparative analysis of the obtained hydration degrees demonstrates the importance of temperature on the hydration process, thus it was observed that the hydration degree for cement pastes hardened at 22 and 38°C is higher than those hardened at 3°C by 3.7% and 8.3% respectively, and by 4.8% for those hardened at 38°C compared to those at 22°C.

3.4 Correlation of mechanical strength with the degree of hydration

This subchapter highlights the link between the mechanical strength and the hydration process in the context of a consensus that the way hydration products appear and form directly influences the mechanical strength.

The effect of hydration temperature on the flexural and compressive strength of mortars was determined experimentally by testing three series of mortar prisms at different ages.

The results obtained show that compressive strength is directly proportional to temperature and the hydration period.

Also, it is clear that higher temperatures lead initially to higher compressive strengths. This behavior has also been reported in other works [2] [7] [14] [21] [28] where it was clearly shown that higher temperatures initially lead to the rapid hydration of Portland cements and high early compressive strengths.

3.4.1 Estimation of compressive strength as a function of time

This subchapter analyzes the evolution of the compressive strength of materials over time, with emphasis on the methods used for estimating it based on empirical or theoretical models. The aim is to identify functional relationships between time and strength, useful in the design and evaluation of long-term structural behavior.

The result of applying mathematical models confirms that the development of the compressive strength can be accurately described by an exponential function such as the one proposed by Zhang *et al* [29] or by an appropriate hyperbolic function. In both cases, the coefficient of determination R^2 presents a value above the threshold of 0.94, with a slightly higher value for the exponential function.

3.4.2 Estimation of compressive strength based on maturity index/equivalent age

This section deals with an advanced and more realistic method of estimating the compressive strength of cementitious materials, taking into account not only the chronological age (number of days since casting), but also the actual thermal conditions to which the material has been exposed. In this regard, the concept of maturity or equivalent age is introduced, which correlates temperature and time to provide a more accurate assessment of strength development.

The compressive strength of concrete is strongly influenced by temperature. At higher temperatures, the hydration reactions of cement accelerate, leading to faster hardening. Maturity is a parameter that integrates time and temperature to evaluate the degree of hydration of mortars, by a method known as the Nurse-Saul method, which is frequently used in practice to monitor maturity.

The equivalent age is a transformation of maturity into a "theoretical age" corresponding to a standard temperature (usually 20°C). It can be calculated with more sophisticated relationships, such as that proposed by Freiesleben Hansen and Pedersen [30], which takes into account temperature variations more realistically, using an exponential formula.

For determining the equivalent age, it was necessary to determine the values of the E_a/R ratio, values obtained by the method developed by Zang *et al* [29] and an exponential equation used in studies such as those by Mariak *et al.* [28], Da-jiang *et al.* [31] and Carino and Lew [30].

Using these values resulted in a maturity index of 0.35 for samples hydrated at 3°C, 1.12 for samples hydrated at 22°C temperature and 2.66 for samples hydrated at 38°C temperature, relative to a reference sample hydrated at 20°C temperature.

The effect of applying these factors to hydration periods is graphically represented in Figure 3-5, where it can be noticed that a 90-day hydration period at a temperature of 3°C corresponds to an equivalent age of 30 days, while for a sample hydrated for the same 90-day period, but at a temperature of 38°C, it corresponds to an equivalent age of 238/248 days.

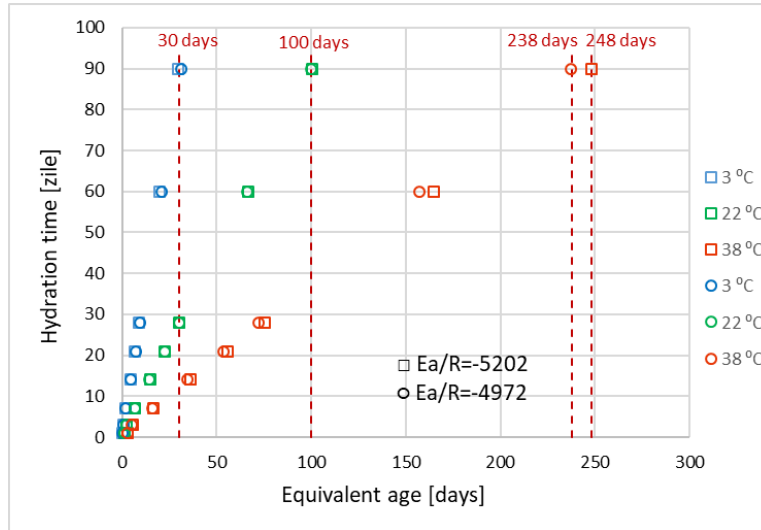


Figure 3-5. Hydration period versus equivalent age

At the same time, a comparative study was carried out between the values of compressive strength determined experimentally and those estimated using the exponential equation describing the strength-age relationship mentioned above. The study is graphically represented in Figure 3-6 and it can be seen that the best estimates were those of the strengths of the samples hydrated at 3°C, but for the other hydration temperatures the estimates were also reasonable, with errors reaching a maximum of 10%.

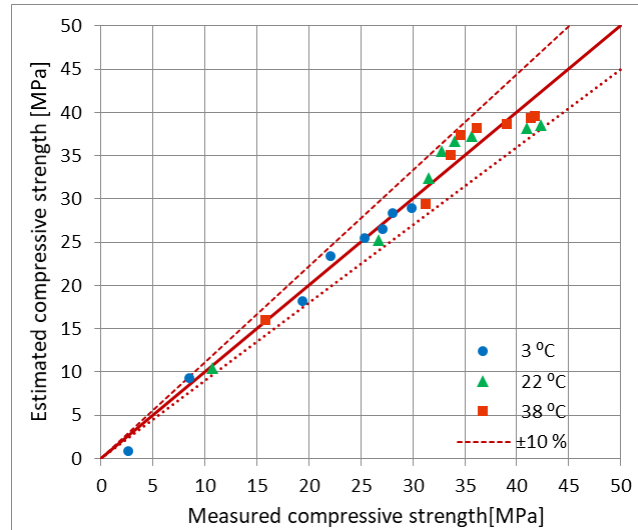


Figure 3-6. Compressive strength – estimated versus measured.

Within the thesis, several equations and mathematical models were processed and applied that describe the relationship between strength and equivalent age with the aim of establishing which of them best fits the experimentally determined results, the conclusions being that the highest determination factor (R^2) was obtained for the case of hydrated mortars at a temperature

of 3°C, all applied functions having values above 0.94 with the lowest determination factor for the power function.

Figure 3-7 presents the graphical representations resulting from the mathematical modeling of these functions that describe the relationship between resistance and equivalent age with the aim of determining which of them best fits the experimentally determined results.

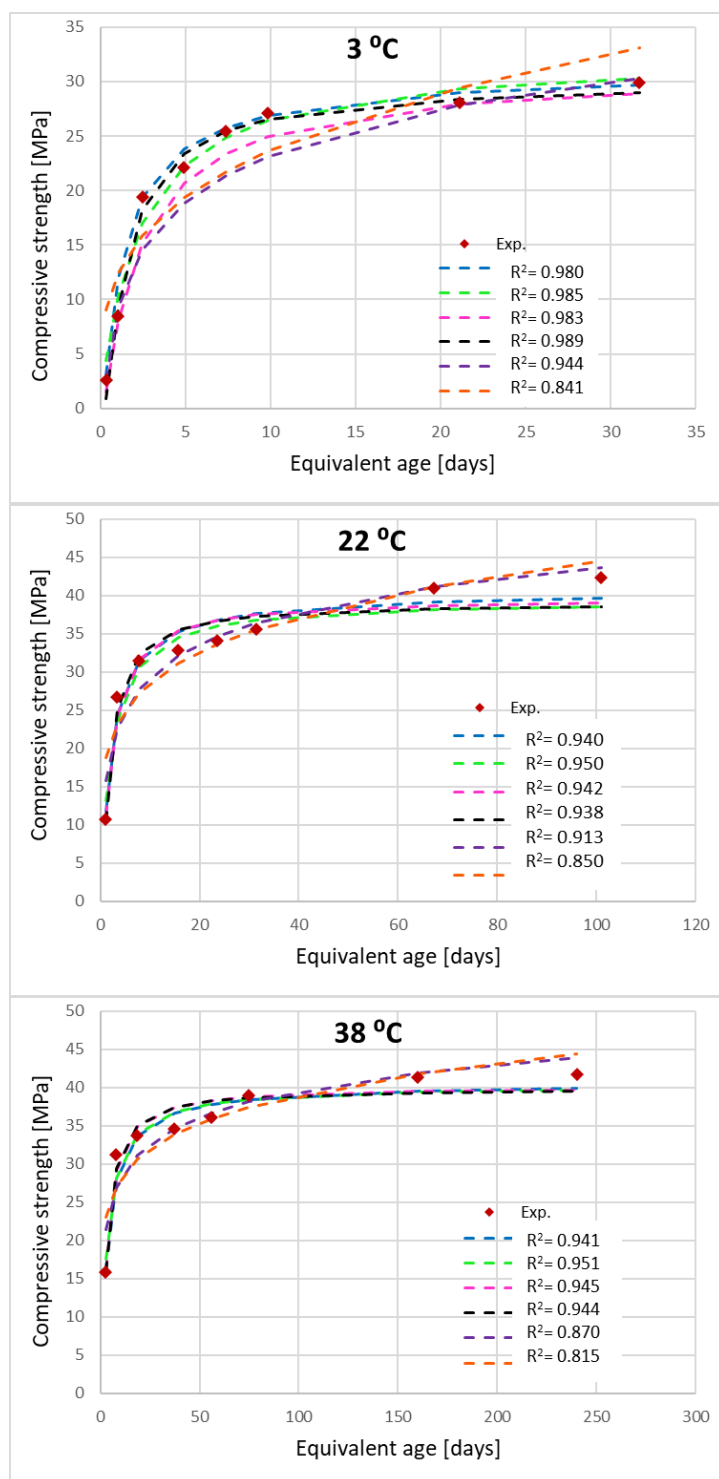


Figure 3-7. Graphical representation of compressive strength, determined experimentally and estimated based on mathematical modeling, in relation to equivalent age and hydration temperature

Here, the maturity curves were also determined, which was achieved by applying the procedure written by Zhang *et al* [29], which states and demonstrates that by choosing the correct value of the apparent activation energy E_a , the three individual curves of the evolution of the compressive strength, determined individually for each of the three hydration temperature levels, will merge into a single curve that will represent the maturity curve.

Using exactly this procedure, two maturity curves were thus obtained as a result of choosing two different values of the apparent activation energy. The graphical representation of the two maturity curves is shown graphically below:

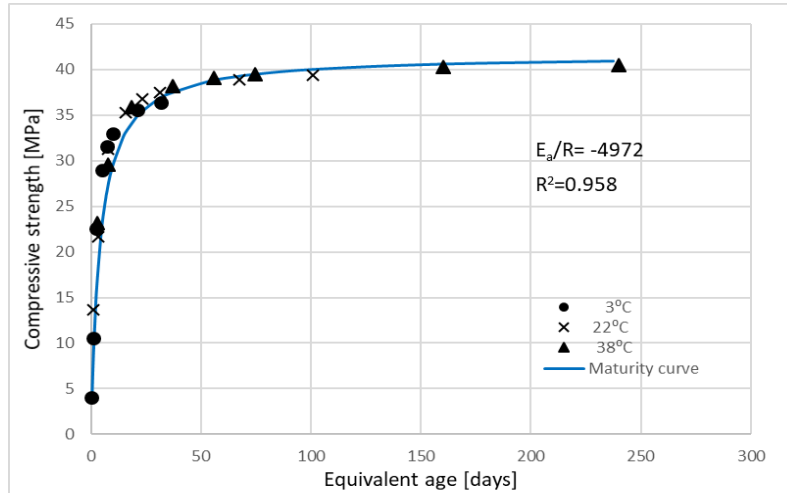


Figure 3-8. Maturity curve using the value of the ratio $E_a/R = -4972$

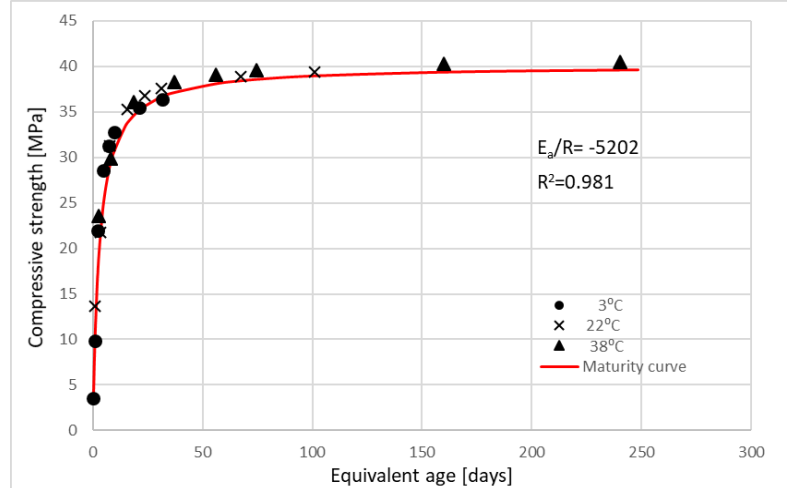


Figure 3-9. Maturity curve using the value of the ratio $E_a/R = -5202$

Analyzing Figure 3-8 and Figure 3-9 it can be observed that for the case of using the ratio value $E_a/R = -5202$ we obtain a better determination factor, but regardless of the method, the correlation factor is $> 0,95$.

3.5 Conclusions

Analyses performed on cement powder using SEM-EDX and ICP-OES techniques allowed for a complex characterization, both morphological and compositional, highlighting in the same time a relatively good correlation between the identification of elements by EDX and their

quantification by ICP-OES, underlining the usefulness of combined analysis for validating and completing information.

At the same time, the use of thermal analyses (DTA/TG) and the appropriate use of mathematical models allowed the quantification and tracking of the evolution of Portlandite and Calcite, a quantification based on which the degree and kinetics of hydration could be estimated, both of cement pastes and of mortars, with the specification that in the case of mortars we cannot predict the degree of hydration based on the estimated Portlandite, since its quantification in the case of mortars does not present the same level of accuracy as in the case of hydrated cement pastes.

The results also demonstrated that the evolution of compressive strength over time can be accurately described by mathematical modeling using an appropriate exponential or hyperbolic function. The correlation with experimental data obtained through actual mechanical strength testing exceeds the value of 0,9.

Regarding the effect of hydration temperature, it is absolutely obvious that both the amount of Portlandite and the strength of concrete increase with the degree of hydration of the cement, and the speed of the hydration reaction increases as a function of time and temperature.

The maturity method is particularly useful in monitoring the strength of mortars and concretes poured in the cold season and in quality control and execution planning based on the actual evolution of mechanical strength.

4 CONSTRUCTION AND RUNNING OF MODELS USED IN THERMODYNAMIC AND KINETIC MODELING OF THE HYDRATION PROCESS

Chapter 4 presents aspects related to process modeling by using software specialized in thermodynamic and geochemical modeling (PHREEQC and GEMS), in order to simulate chemical equilibrium and establish the kinetics of the products resulting from hydration reactions and the integration of experimental data (TGA, XRD, SEM/EDX) for the calibration and validation of the models developed and run using these software tools.

4.1 Modeling the evolution of pore water

This subchapter presents the results of modeling the evolution during the hydration process of the solution in the pores of a cement paste made with the CEM II/B-M cement type, modeling obtained using the GEMS software.

Following the process simulation, it was found that during hydration, significant changes occur in the composition of the solution in the pores of the cement paste, especially on the first day when it was observed that the solution in the pores of the cement paste is dominated by sodium, potassium, sulfur, calcium and hydroxide.

4.2 Development and running of the model used in thermodynamic modeling

This subchapter presents the results of thermodynamic modeling that underlies the prediction and determination of hydration products and solution concentration in the pores of hydrated cement paste.

Thus, using appropriate computational codes (PHREEQC and GEMS), models were built, which, after running them, led to the qualitative and quantitative estimation of hydration products, suggesting the formation of products such as: CSH, Portlandite, Etringite, Hydrotalcite, Hydrogarnet, Ferrihydrite, Monocarbonate and Calcite.

4.3 The development and running of models that simulate cement dissolution and hydration processes

Within the study, a kinetic modeling of the hydration process was performed for a CEM II/B-M composite cement paste, with the aim of simulating the evolution of hydration reactions over time.

For the simulation, the two codes mentioned earlier mineralogical database CEMDATA 18.1 were used, which provides detailed thermodynamic information for the phases involved in the process.

The modeling was based on the kinetic models developed by Parrot and Killoh, recognized for their ability to realistically describe the behavior of the mineral phases in cement during hydration.

Figure 4-1 shows both the kinetics of the hydration process of the four major phases present in this cement and the evolution over time of the degree of hydration. This graphic representation was obtained using the PHREEQC geochemical modeling software.

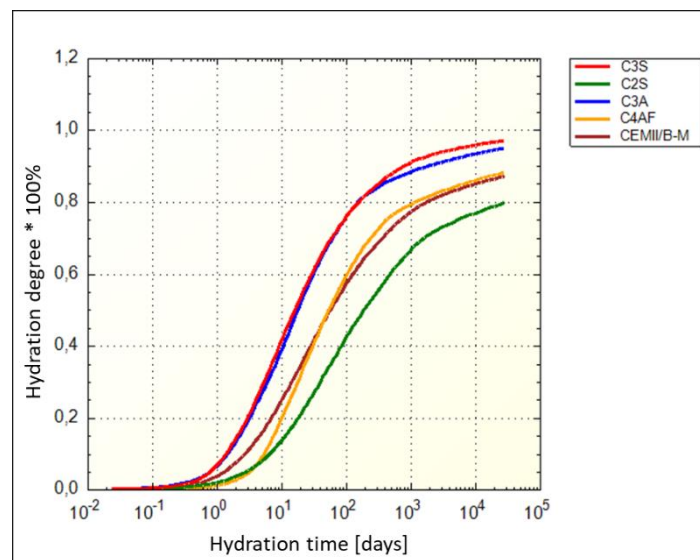


Figure 4-1. Hydration kinetics of the four main phases present in the structure of Portland cement clinker over 28 days.

On the other hand, the use of GEMS software also allowed a graphical representation of the distribution and evolution of the masses of the constituents (phases/hydration products) of the hydrated cement paste, a representation shown in Figure 4-2.

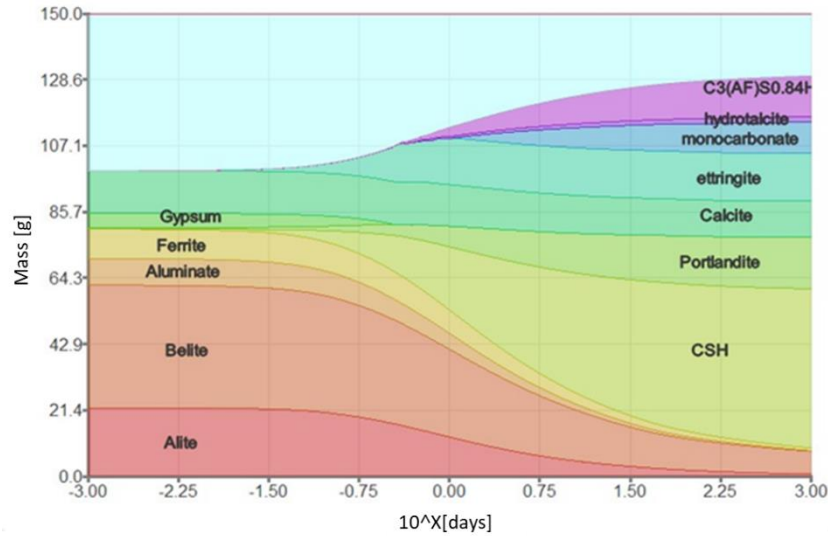


Figure 4-2. The evolution of the mass of clinker phases and the formation of hydration products under the hypothesis of complete hydration of CEM II/B-M (S-LL) type cement

This representation indicates, as it is normal, the formation of the same hydration products as in the thermodynamic modeling.

4.4 Model validation through comparative analyses

In this stage of the research, the aim was to validate the hydration and mineralogical prediction models by comparing simulated results with experimental ones. The main objective was to verify the accuracy of the modeling performed using the GEMS software.

In the comparative analysis of the evolution of the Ca(OH)_2 content, differences were identified between the experimental and simulated data, especially in the initial stage of hydration. In the first part of the graphs, Figure 4-3 and Figure 4-4, a more pronounced deviation between the two data sets is observed, but this difference is significantly reduced as the hydration process progresses.

This discrepancy is attributed to errors in the quantification of calcium hydroxide (Ca(OH)_2) in the early phase of the hydration process, when the hydration product is present in small quantities and measurement errors can have a greater overall impact on the correct estimate.

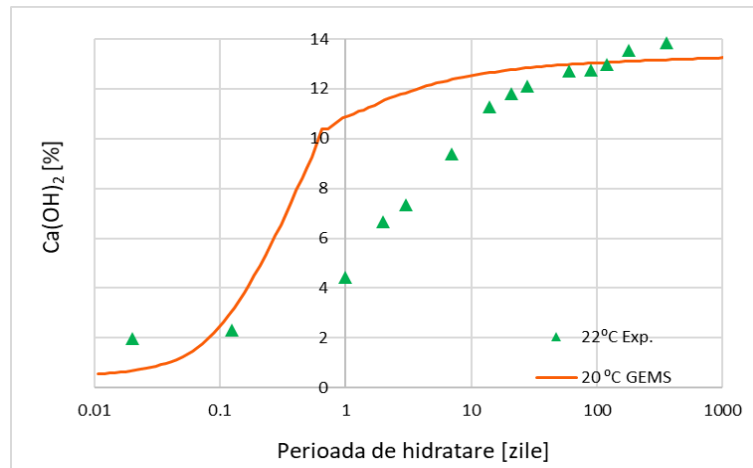


Figure 4-3. Comparative analysis of the evolution of Ca(OH)_2 content in a cement paste

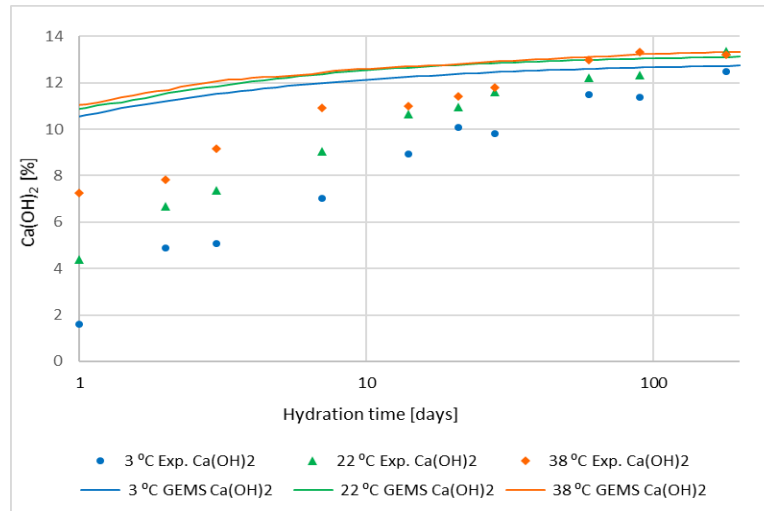


Figure 4-4. Comparative analysis of Portlandite content in cement pastes hydrated at different

In contrast, in the case of cement paste hydration kinetics, it is shown that the experimental results overlap quite well, Figure 4-5 and Figure 4-6, with those obtained by modeling. This statement is also supported by the high values of the coefficient of determination (R^2).

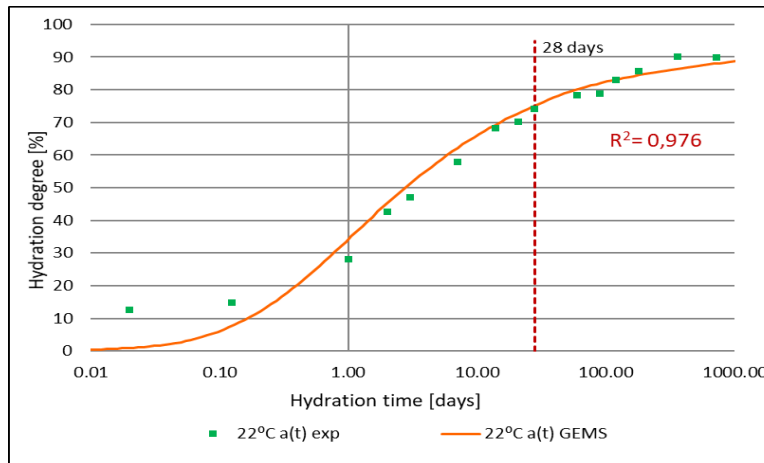


Figure 4-5. Comparative analysis of hydration kinetics

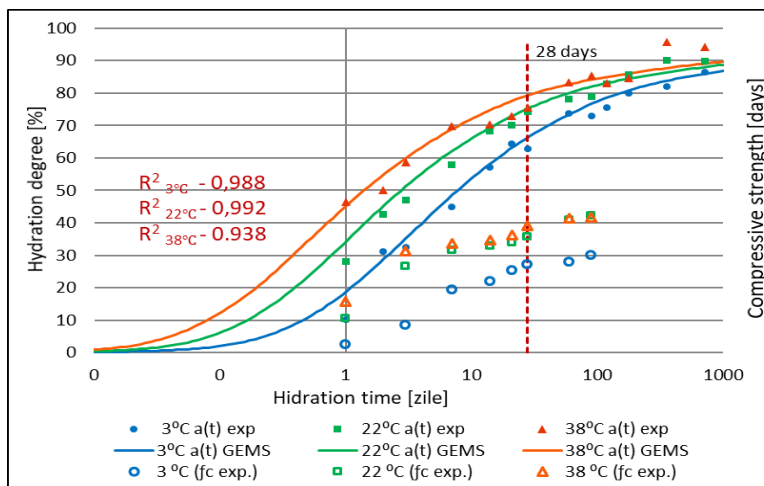


Figure 4-6. Comparative studies highlighting the relationship between mechanical strength versus the degree and temperature of hydration

Furthermore, the comparative studies carried out and presented in Figure 4-6 show that by superimposing the data obtained from mechanical strength tests, it is obvious that the compressive strength of concrete increases with the degree of hydration of the cement, and the reaction rate and the degree of hydration increase with temperature. It is this dependence that makes it possible to describe and represent the evolution of mechanical strength as a function combining the effects of time and temperature by using the maturity index [7] [29] [28].

4.5 Conclusions

Thermodynamic modeling using the two software allows for a good quantitative and qualitative estimation of hydration products, all approaches indicating both the formation of the same main hydration products and their similar masses, unlike the quantitative estimation obtained using ternary diagrams where it can be observed that there is some difference in the quantitative estimation of the phases, compared to that obtained using geochemical modeling software, differences caused by the fact that this method cannot accurately assess the changes in solid phases generated by variations in temperature, humidity and the presence of some gases.

The use of PHREEQC and GEMS codes allowed for the graphical representation of the evolution of the dissolution and hydration processes and at the same time the distribution and evolution of the masses and volumes of the constituents (phases/hydration products) of the hardened cement paste.

At the same time, the results showed that there is a relatively good agreement between the cement hydration kinetics, based on Portlandite quantification obtained through thermal analysis (DTA/TGA), and the hydration kinetics obtained using the Parrot and Killoh model, as well as geochemical codes.

The conclusion that emerges is that, despite some initial differences, the implemented models manage to faithfully reproduce the evolution of the hydration process, strengthening its validity and utility in predicting the mineralogical behavior of cement pastes on the long term.

5 ANALYSES AND EXPERIMENTAL STUDIES ON THE EVOLUTION OF MORTAR PROPERTIES IN VARIOUS ENVIRONMENTAL CONDITIONS

Chapter 5 highlights the impact generated by the physicochemical interactions that occur between cement-based systems and the various environments with which they may come into contact.

In this context, several processes and interactions were reproduced and analyses and tests were performed to highlight the impact that these interactions and processes can have on the stability and physical, chemical and mechanical integrity of cement-based structures.

5.1 Simulation of the leaching process

In this subchapter, the interaction between cement-based materials and potentially infiltrated waters from the host environment was investigated, a laboratory experiment was designed and it involved the controlled exposure of samples to simulated chemical solutions. The aim was to

evaluate the durability and chemical stability of the materials under conditions that mimic the real storage environment (e.g. in the context of radioactive waste repositories or engineered barriers).

In this regard, three synthetic solutions were prepared, reflecting the chemical composition of the groundwater from the host environment "Saligny Water 1", "Saligny Water 2", and the MgSO_4 solution.

For comparison, a set of samples stored under reference conditions, called APC (simulated cement water), was included. These samples were maintained in a lixiviant designed to simulate the composition of the water in the pores of the cement material.

The APC solution is a hyperalkaline solution, formulated according to the model proposed by Wieland and Van Loon [32].

5.2 Analyses of samples subjected to the leaching process

This section presents the results obtained from analyses performed on samples subjected to the leaching process. The aim of the analyses was to evaluate the chemical behavior and mineralogical stability of cement pastes under conditions similar to those encountered in the storage environment.

During the leaching experiment, a number of significant phenomena were observed that provide important clues about the interaction between the cement paste and the simulated chemical solutions.

From the early stages of the test, a low concentration of calcium in the solution was observed, probably attributed to residual calcium oxides (CaO) and not to the dissolution of calcium hydroxide ($\text{Ca}(\text{OH})_2$). This hypothesis is supported by the pH values recorded, which did not fall below the critical threshold required for the dissolution of $\text{Ca}(\text{OH})_2$, thus maintaining a stable hyperalkaline environment.

After approximately 90 days, a sudden decrease in the concentrations of Na^+ , K^+ and Ca^{2+} in the solution was observed, accompanied by the formation of a visible precipitate and a slight increase in the content of Si^{4+} . This evolution suggests the formation of poorly soluble carbonates or bicarbonates. The formation of these insoluble compounds would explain the decrease in the concentration of cations and the reduction of the basicity of the solution (through the consumption of alkali ions), a phenomenon also reflected in the evolution of the pH.

The precipitate formed was collected and stored for further analysis, but due to logistical and time reasons, it could not be subjected to the chemical digestion process at this stage of the study. At the same time, ICP-OES (inductively coupled plasma optical emission spectrometry) analyses for the samples from the other liquid solutions have not yet been performed, representing future research directions to complete the interpretations regarding the leaching mechanisms and chemical stability of the system.

This set of observations highlights the complexity of chemical processes at the cement-solution interface and reveals the essential role of the composition of the liquid medium in determining the long-term behavior of cementitious materials. Phenomena such as selective dissolution, the

formation of new phases, and pH variations provide useful information for assessing the evolution and stability of these materials under real environmental conditions.

On the other hand, pH analyses performed on mortars subjected to the leaching process for a period of 720 days demonstrate that its value is above the threshold for initiating the Ca(OH)_2 dissolution process, a process which according to Lagerblad [3] occurs at a $\text{pH} \geq 12$.

The results of thermogravimetric analyses do not indicate major differences in the evolution of Ca(OH)_2 and CaCO_3 for any of the samples subjected to the leaching process for a period of 720 days, however, the estimation of the amount of Ca(OH)_2 based on the TGA curves indicates a slight decrease in its amount in the samples subjected to leaching.

From the analysis of the XRD spectra, it is found that in addition to Portlandite, the presence of Calcite, Quartz, Ettringite and C-S-H (Calcium Silicate Hydrate) is also observed, and for the samples subjected to the sulfate attack, the presence of gypsum and carbonates in the form of $\text{MgCO}_3 \cdot \text{CaCO}_3 \cdot \text{H}_2\text{O}$ is also observed.

SEM images and EDX diagrams for samples that come into contact with cement water and Saligny 1 water show that the analyzed samples do not show changes in terms of chemical and mineralogical composition, the main hydration products are still present in these samples, especially those containing Ca.

In the case of samples subjected to leaching with Saligny 2 water and sulfate attack, a higher presence of aluminum was found, which may indicate the formation of late Ettringite, and the presence of magnesium was also found, which may suggest an initiation of the process of sulfate attack and formation of brucite, a compound that can generate expansions, but following the measurements carried out, no changes of this kind were reported.

The mechanical strength tests results show an upward evolution of this property proportional to the hydration period, followed by reaching a plateau, with a small exception in the case of samples subjected to the leaching process using the MgSO_4 solution as the percolating liquid, whose strength seems to suffer a regression after 360 days of exposure.

5.3 Simulation of the accelerated decalcification process

This subchapter aimed to accelerate the decalcification process of cement pastes, in order to highlight more clearly the chemical and structural effects of calcium ion loss, in a shorter time frame than in the case of conventional leaching tests.

To simulate this process in an accelerated manner and obtain relevant results in a shorter time frame, it was chosen a method established in the specialized literature: exposing the samples to an ammonium nitrate solution (NH_4NO_3).

Following the analysis of the solutions by ICP-OES, an increase in Ca concentration was identified, a fact also supported by the pH values which decreased directly proportionally to the immersion time of the samples.

Regarding the structural changes, DTA/TGA differential thermal analyses indicate that after 60 days in contact with the ammonium nitrate solution, the Ca(OH)_2 phase is no longer found in the analyzed samples, demonstrating the release of Portlandite under these accelerated

conditions, with a direct effect on the reduction of mechanical strength, the value of which is inversely proportional to the immersion time in the ammonium nitrate solution.

Another important observation of these tests is that the compressive strength of samples with a w/c ratio = 0,5 is significantly higher than those with a w/c ratio = 0,65, and under conditions of chemical attack (which simulates accelerated degradation), the decrease in strength of samples prepared with a w/c ratio = 0,5 is more pronounced/greater than that of samples prepared with a ratio of 0,65.

5.4 Simulation of carbonation processes

This chapter investigated the effects generated by the exposure of cement-based materials to two sources of CO₂, one with a concentration of 1%, and the other at the concentration at which CO₂ is normally found in the air, 0,06÷0,07%.

The evolution of the thickness of the degraded layer over the two years in which the process was monitored highlights the fact that the CO₂ front from the air uniformly penetrates the sample compared to that from the artificial source, and also tends to be smaller.

The penetration depth of the CO₂ front was revealed using the classical phenolphthalein testing method (Figure 5-1) and through thermogravimetric analyses, with the results graphically represented in Figure 5-2, where the same trend is observed. Additionally, the EDX analyses appear to indicate a lower carbon content in the samples subjected to carbonation in air, while the XRD diagrams identify more calcite positions in the samples exposed to CO₂ from the artificial source.



Figure 5-1. Determination of the carbonated layer thickness using phenolphthalein, two years after the initiation of the process

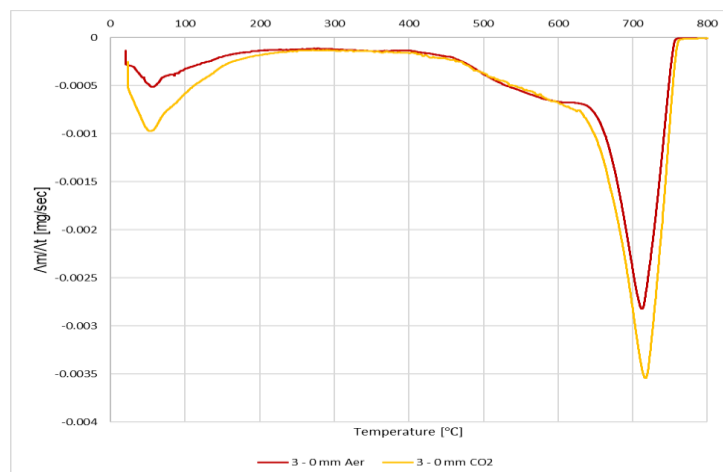


Figure 5-2. Graphical representation of first-order derivatives (DrTGA), comparing the two CO₂ sources

Regarding the evolution of pH in the samples, the values are close to those of the reference sample, which is partly explained by the fact that CaCO_3 does not react with the pure water with which it was put in contact, so that this leads to a reduction in pH.

Regarding the impact of carbonation on the evolution of mechanical strength, the results indicate, regardless of the source, that the strength of exposed mortars tends to be higher compared to that of the reference samples.

6 MODELING THE EFFECTS OF DEGRADATION PROCESSES ON THE EVOLUTION OF PORE WATER AND ON HYDRATION PRODUCTS

Chapter 6 integrates advanced numerical and geochemical modeling methods to analyze the impact of degradation processes (leaching, carbonation) on the composition of pore water and on the solid hydration phases in cement paste. The modeling was performed using specialized software, mainly PHREEQC and GEMS, in order to evaluate the chemical changes that occur following the interaction of cementitious materials with different aggressive environments.

6.1.1 Carbonation

This subsection was dedicated to simulating contact with CO_2 . The first model simulated the gradual penetration of CO_2 into the solution from the pores of cement pastes, the maximum amount added reaching the concentration value at which CO_2 is normally found in the air (~700 ppm).

This reaction of carbon dioxide with the solution primarily leads to increased calcium dissolution and the formation of calcium carbonate, as can be seen in Figure 6-1, but a decrease in Na concentration was also recorded, which led to the formation of sodium carbonate as can be seen in Figure 6-2, both accompanied by a decrease in pH.

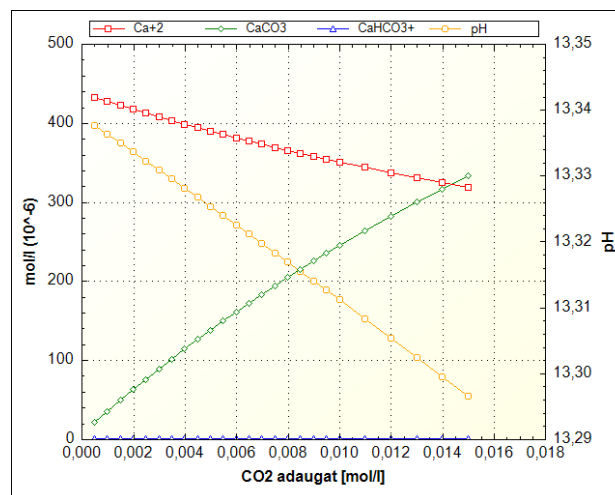


Figure 6-1. Dissolution of Ca and formation of CaCO_3 as a result of CO_2 penetration

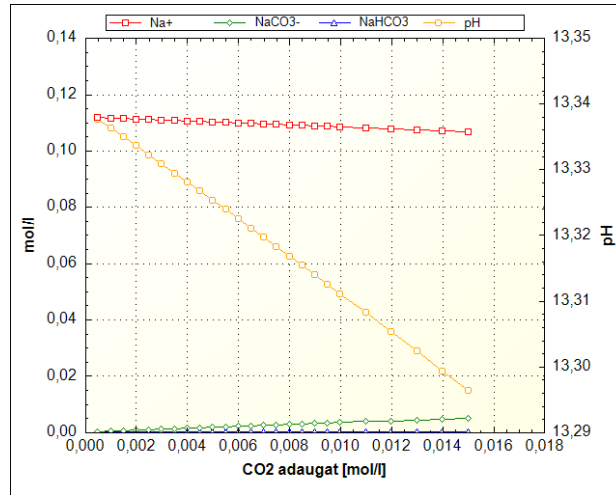


Figure 6-2. Dissolution of Na and formation of NaCO_3 as a result of CO_2 penetration

The second model consisted in mixing some water in which CO_2 was dissolved with the solution in the pores of the cement pastes. The carbonated water (ac)/pore solution (sp) ratio was 1:9, and the pressure at which the gas dissolution occurred was set to the value specified in the specialized literature [4] [33], which states that the partial pressure/fugacity of the gas, $\text{CO}_2/(\text{PCO}_2)$ in this case, dissolved in water corresponds to the atmospheric value $10^{-3.4} \div 10^{-3.5}$ atm.

The graphical representation of the results obtained from running this model is shown in Figure 6-3.

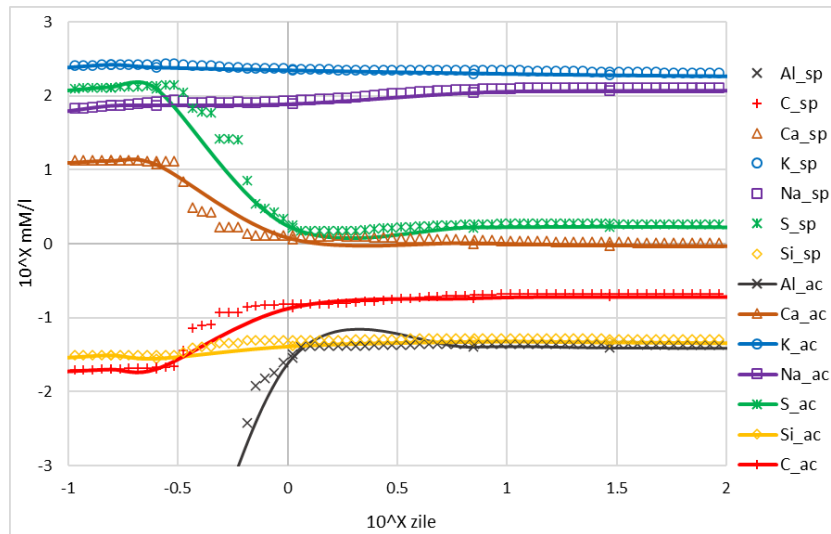


Figure 6-3. The evolution of the chemical composition of the pore solution (sp) of CEM II cement paste following contact with carbonated water (ac) using the PHREEQC software

It can be seen that in the presence of carbonated water the concentration of ions in the solution does not seem to be significantly influenced in any of the cases, which is to be expected considering the mixing ratio of the two solutions.

6.1.2 Leaching

This section was dedicated to simulating the effect of leaching on both the pore solution of a cement paste and the hydration products.

To highlight the effects of such a process, a model was built based on the hypothesis of water penetration into the system, followed by the displacement of up to 50% of the total volume of the solution from the pores of the hydrated cement pastes.

The graphical representation of the results obtained from running this model is shown in Figure 6-4.

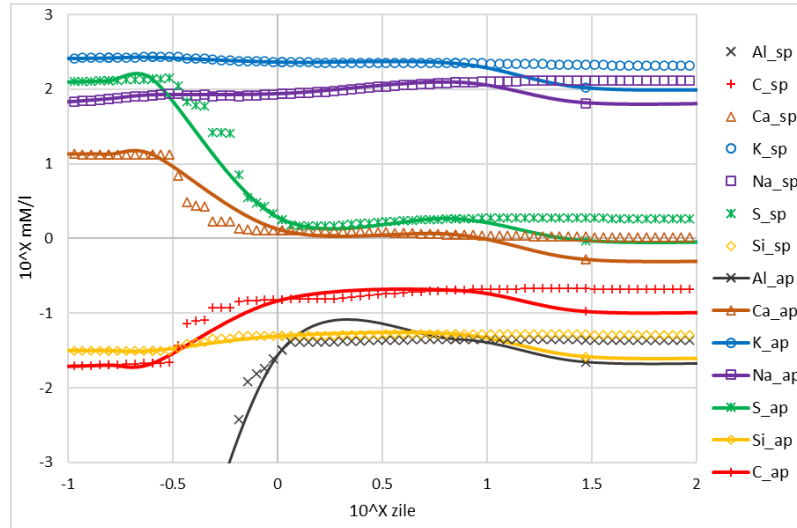


Figure 6-4. The evolution of the chemical composition of the pore solution (sp) of CEM II cement paste following the simulation of leaching with pure water (ap) using the PHREEQC software

It can be seen that in the presence of water, the concentration of ions in the solution is disturbed, registering a significant decrease, which is to be expected considering the percentage of dislocation, which practically led to a dilution of the ion concentration.

The graphical representation of the results for the cement paste leaching case is shown graphically in Figure 6-5.

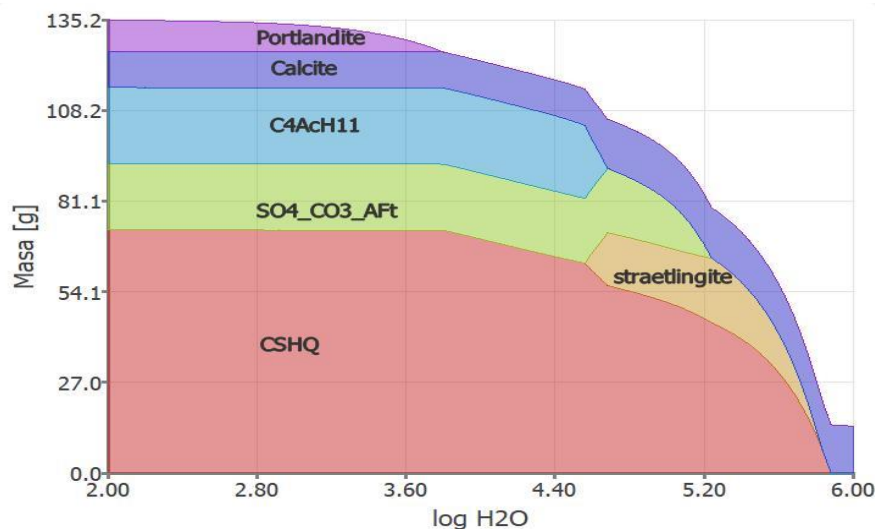


Figure 6-5. The evolution of the main hydration products as a result of simulating the leaching process with pure water using GEMS software

In the case of water infiltration into the structure of a cement paste, the undesirable effect generated by this process can be observed, which first leads to the destabilization of Portlandite,

followed by that of CSH, simultaneously with the appearance of strätlingite, caused by the reduction of the Ca/Si ratio and the amount of SO_4^{2-} .

6.2 Conclusions

Computer modeling of degradation processes using PHREEQC and GEMS software has demonstrated that these tools are essential for understanding the complex interactions between cement solids and pore water under various environmental conditions. The simulations confirm that the internal chemical equilibrium is dynamic and sensitive to changes imposed by external factors, which directly influences the long-term stability of cementitious materials. Thus, the integration of numerical modeling methods becomes an indispensable tool in advanced research on the durability of construction materials.

7 ANALYSES ON WATER MOBILITY AND RETAINMENT ON AND MOVEMENT THROUGH MORTAR OF RADIONUCLIDES

The study described in this chapter aimed to investigate the hydrodynamic behavior of water and the mobility of radionuclides through mortars, in order to evaluate the efficiency of these materials in retaining contaminants and consequently delaying their release from the storage area.

7.1 Porosity and permeability tests

This subchapter aimed to determine the effective porosity and permeability of mortars, two essential properties that directly influence the durability, freeze-thaw resistance and behavior over time of the structure. The tests were performed for objective reasons only on undegraded samples.

Thus, based on the methodology recommended by the International Society for Rock Mechanics (ISRM) [34], a value was obtained $\eta_{\text{efectivă}} = 8.77\%$, the vast majority of values for mortars being in the range of $10 \div 20\%$ [35] [36].

On the other hand, analyses performed using a mercury intrusion porosimetry (MIP) indicate that the material has a very dense and homogeneous microstructure, with a large number of pores with dimensions between 6 and 10 nm, which translates into low permeability and good durability.

The permeability tests were performed using a facility designed and built within the Institute for Nuclear Research Pitesti, the results obtained indicating permeability values in the range $1.8\text{E}-13 \div 4.74\text{E}-13$, values similar to those reported by Neville [37] for well-compacted and hydrated mortars.

7.2 Sorption tests on mortar matrices

This subchapter deals with the behavior of undegraded/degraded mortar matrices with regard to capillary sorption, a process essential for understanding how dissolved contaminants (in this case ^{137}Cs and ^{90}Sr) are absorbed and transported into the internal structure of porous materials.

Sorption tests are based on the *batch* experimental method which consists of mixing a solution containing the dissolved contaminant with a well-defined amount of solid phase (sorbent matrix), under controlled conditions of time, temperature and pH, in order to determine the moment when sorption equilibrium is reached (assumed to be the moment when the sorption rate is equal to the desorption rate) in order to calculate the distribution coefficient K_d .

Figure 7-1 presents the kinetics of ^{137}Cs sorption on the six mortars studied. The analysis of the graph shows that after 48 hours of contact between the two phases, equilibrium in solution was not reached for all six systems.

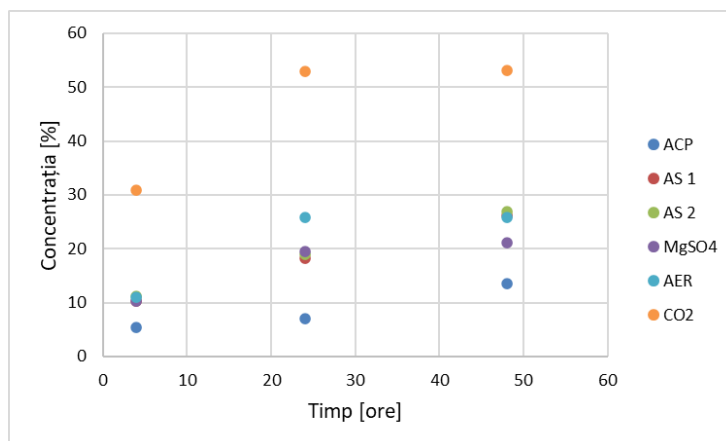


Figure 7-1. Kinetics of ^{137}Cs sorption on mortar systems

Therefore, the correlation of experimental data with linear sorption isotherms in order to determine the sorption coefficient K_d can only be applied to systems that have reached equilibrium, which is why for the other systems the distribution ratio R_d was determined, which is mainly used in the literature instead of K_d for systems that have not reached sorption equilibrium.

To test the correlation of the results obtained, for systems that have reached equilibrium, with the linear sorption isotherm, in Figure 7-2 the concentration of the contaminant sorbed on the solid matrix was plotted as a function of the concentration of the contaminant in the solution, at equilibrium, the distribution coefficient being the slope of each of the represented lines.

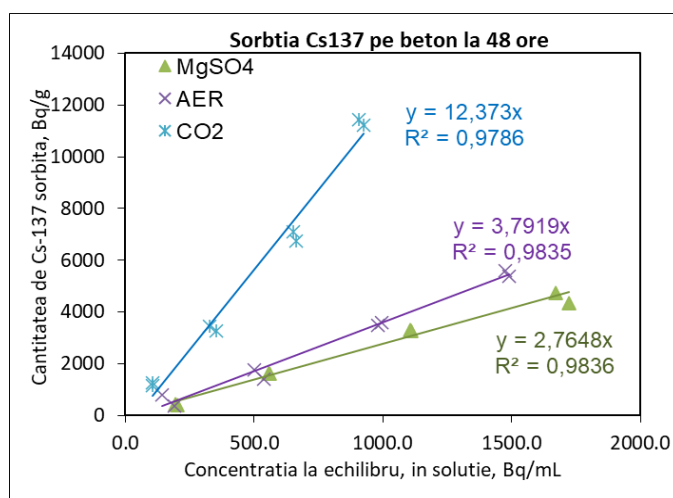


Figure 7-2. Linear ^{137}Cs sorption isotherms for systems that have reached equilibrium

The sorption model shows high accuracy with respect to the experimental data, as indicated by the values of the correlation coefficients.

The values of the cesium distribution coefficients, determined from the slope of the line, fall within the range of values found in the specialized literature, for cement-based systems generally reported values between $1 \div 10$ [38] [39] [40].

The more efficient sorption of cesium (Cs^+) on carbonated mortar compared to sorption on other mortars is explained by the chemical and structural changes that occur during the carbonation process of concrete, the formation of new phases with high sorption capacity, a lower pH (favorable for the sorption of monovalent ions), and less competition for sorption sites.

Figure 7-3 shows the kinetics of ^{90}Sr sorption on the six mortars studied. From the analysis of the graph it appears that after 90 hours of contact of the two phases, equilibrium in the solution was reached for four of the six systems, in samples AS 1 and AS 2 it seems that sorption continues.

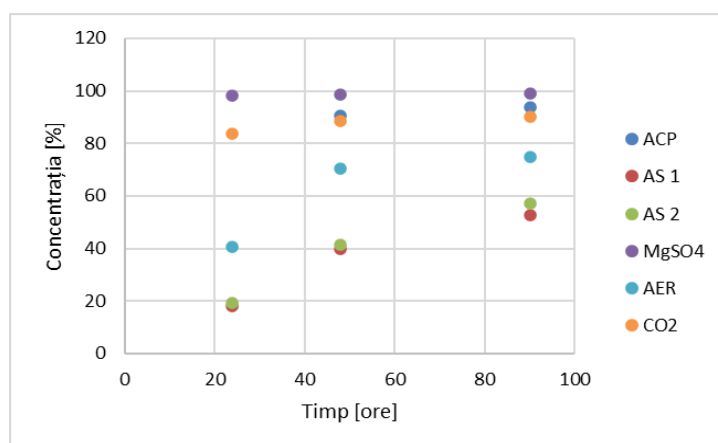


Figure 7-3. Kinetics of ^{90}Sr sorption on mortar systems

The correlation of the results obtained with the linear sorption isotherms for the case of using ^{90}Sr is graphically represented in Figure 7-4, where it can be observed that in this case the distribution coefficient K_d with the highest value is the one recorded on the samples that were maintained in ACP cement water.

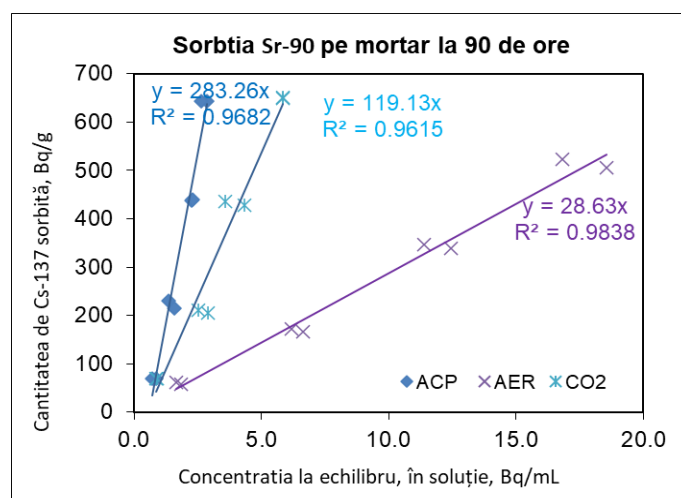


Figure 7-4. Linear sorption isotherms of ^{90}Sr for systems that have reached equilibrium

The correlation factors of the experimental data with this sorption model, in the case of using the ^{90}Sr contaminant, are above the value of 0,96, which indicates a relatively good correlation.

The values of the ^{90}Sr distribution coefficients, determined from the slope of the line, fall within the range of values found in the specialized literature, which specifies for cement-based systems with $\text{pH} > 12.5$ values between 100÷500 [41] [42], and for carbonate systems with lower pH values below 100 [42].

Figure 7-5 confirms that the samples for which it was obtained a high value of the distribution coefficient are in a hyperalkaline environment, in which the hydration products are found in their entirety, while the samples subjected to carbonation have a $\text{pH} \leq 12$, a value at which phases with sorption potential of ^{90}Sr such as Portlandite began to degrade.

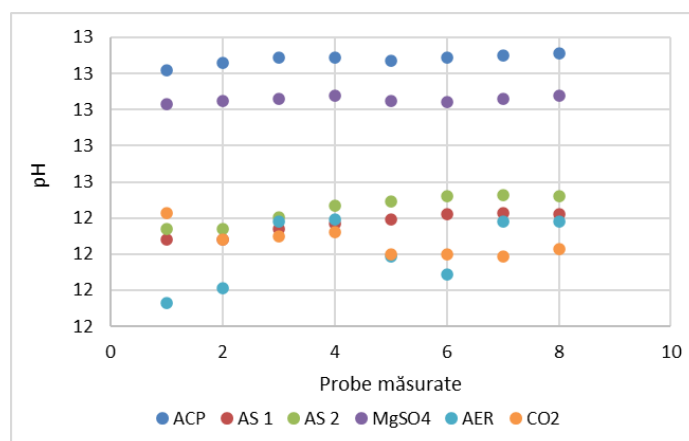


Figure 7-5. pH of samples that were in contact with the ^{90}Sr -labeled solution for 48 hours

7.3 Conclusions

Porosity and permeability tests demonstrated that the values of the two properties are within the range of values specific to well-compacted and hydrated mortars.

Sorption tests showed that the values of the distribution coefficient of ^{137}Cs are higher in the case affected by the carbonation process, while for ^{90}Sr the distribution coefficient is higher on matrices that have not undergone degradation.

The sorption of ^{137}Cs on mortars is relatively low, mainly due to the presence of Na^+ and K^+ ions in the undegraded mortars, but it can be observed that as these ions leave the system, as in the case of samples subjected to the leaching process, the distribution coefficient shows increasing values. However, the highest values of the distribution factor were recorded for the case of mortars subjected to accelerated carbonation, which is most likely due to the formation of new phases with high sorption capacity.

Regarding ^{90}Sr sorption, it presents significantly higher distribution coefficients compared to ^{137}Cs , due to the fact that it possesses a chemical character similar to calcium (Ca^{2+}), which gives it a greater affinity for cement-based matrices.

8 CONCLUSIONS

This paper provides a complex and integrated analysis of the behavior of cement-based materials (especially **CEM II/B-M**) widely used in engineered barrier systems within radioactive waste disposal systems, focusing on **chemical composition, hydration, degradation processes and transport properties**.

The results obtained highlight the following essential aspects:

- Thermal analyses (DTA/TG), correlated with appropriate mathematical models, allowed the quantification of Portlandite (Ca(OH)_2) and Calcite (CaCO_3) phases, data subsequently used to estimate the degree and kinetics of hydration of cement pastes and mortars. This methodology obtained a good precision estimate of the degree of hydration in the case of cement pastes, but the estimation of the degree of hydration of mortars based on the amount of Portlandite is less precise compared to that obtained for hardened cement pastes, due to the additional influence exerted by the presence of aggregates.
- Regarding the influence of temperature on the hydration process, it was found that both the formation of Portlandite and the increase in mechanical strength are directly proportional to the degree of hydration, hydration whose reaction rate increases significantly with hydration time and temperature. This functional relationship between time, temperature and strength evolution allows the application of the maturity method for the precise estimation of the strength of cement-based materials under real conditions (in-situ).
- The maturity method is particularly useful in monitoring the strength of mortars and concretes poured in the cold season and quality control and execution planning based on the actual evolution of mechanical strength.
- The evolution of compressive strength as a function of time was accurately described by exponential or hyperbolic functions, obtaining a very good correlation between the experimental values and those obtained by modeling with mathematical functions.
- Thermodynamic modeling using the two software allows for a good quantitative and qualitative estimation of hydration products, both approaches indicating both the formation of the same main hydration products and their similar masses.
- The use of PHREEQC and GEMS codes allowed for the graphical representation of the evolution of the dissolution and hydration processes and at the same time the distribution and evolution of the masses and volumes of the constituents (phases/hydration products) of the hardened cement paste.
- In comparative studies, the results showed that there is a relatively good agreement between the cement hydration kinetics, based on the quantification of Portlandite by thermal analysis (DTA/TGA) and the hydration kinetics obtained using the Parrot and Killoh model, as well as geochemical codes.
- Chemical degradation of mortars, simulated by processes such as leaching, carbonation and accelerated decalcification, demonstrated the impact of these processes on the mineral composition, pH and mechanical properties. These processes lead to the

dissolution and transformation of products such as NaOH, KOH and Ca(OH)_2 and the formation of new carbonate or sulfate compounds.

- In relation to the structural changes induced by the simulated leaching processes, DTA/TGA, XRD and EDX analyses indicate the existence of Portlandite in the material structure, which leads us to conclude that this process is a slow one, without major effects on the mechanical resistance, in the first years after the installation. Experimental leaching tests show that by immersing mortars and concretes in not very aggressive solutions, such as simulated Saligny 1 and 2 or sulfate waters, Portlandite in the composition of these materials is not significantly leached from the matrix, on the other hand in accelerated decalcification processes, simulated by immersion in ammonium nitrate solution (NH_4NO_3), both Portlandite (Ca(OH)_2) and C-S-H are affected as a result of the leaching of calcium and hydroxide ions. ICP-OES analyses revealed a progressive increase in the Ca concentration in the solution, signaling the advancement of the Portlandite dissolution front. The kinetics of calcium release is directly proportional to the water/cement ratio (w/c) and the exposure time.
- Thermal DTA/TGA analyses showed that, after 60 days of contact with the NH_4NO_3 solution, Portlandite almost completely disappears from the matrix. Regarding mechanical properties, although the samples with w/c ratio = 0.5 present a higher initial strength compared to those with w/c ratio = 0.65, in the case of the accelerated decalcification process, the decrease in compressive strength is more pronounced for the samples with a/c = 0.5. This is most likely explained by the higher initial content of Portlandite available for the reaction, the loss of which leads to an increase in porosity and implicitly to a more pronounced decrease in mechanical performance.
- Regarding carbonation processes, both methods of estimating the attack have highlighted the fact that as we approach the surface, the amount of Ca(OH)_2 decreases simultaneously with the increase in the amount of CaCO_3 , reaching the point where at the surface (0-3 mm depth) the conversion is almost complete, with a higher share for the case of accelerated carbonation.
- On the other hand, the pH values are close to those of the reference sample, which is partly explained by the fact that CaCO_3 does not react with the pure water with which it was put in contact, so that this leads to a reduction in pH.
- Regarding the impact of carbonation on the evolution of mechanical strength, the results confirm a higher strength of the exposed mortars even than the standard ones. At the same time, the sorption tests demonstrated that the mortars affected by carbonation possess higher sorption capacities than the other mortars studied, for both radionuclides used in the study.
- Computer modeling of degradation processes using PHREEQC and GEMS software has demonstrated that these tools are essential for understanding the complex interactions between cement solids and pore water under various environmental conditions. The simulations confirm that the internal chemical equilibrium is dynamic and sensitive to changes imposed by external factors, which directly influences the long-term stability of cementitious materials. Thus, the integration of numerical modeling

methods becomes an indispensable tool in advanced research on the durability of construction materials.

- Porosity and permeability tests demonstrated that the values of the two properties are within the range of values specific to well-compacted and hydrated mortars.
- Regarding the sorption experiments performed, they highlighted the fact that the sorption of ^{137}Cs on mortars is relatively low, mainly due to the presence of Na^+ and K^+ ions in the undegraded mortars, but it can be observed that as these ions leave the system as in the case of samples subjected to leaching processes, the distribution coefficient shows increasing values. However, the highest values of the distribution factor were recorded in the case of mortars subjected to accelerated carbonation, which is most likely due to the formation of new phases with good sorption capacity for cesium.
- Regarding the sorption of ^{90}Sr , sorption tests have shown that this radionuclide has distribution coefficients significantly higher than those obtained for cesium, due to the fact that it possesses a chemical character similar to calcium (Ca^{2+}), which gives it a greater affinity for cement-based matrices.
- At the same time, sorption tests showed that the sorption of radionuclides ^{137}Cs and ^{90}Sr on the cement-based matrix shows similar behaviors in terms of kinetics, despite the distinct chemical nature of the two ions and the dominant interaction mechanisms with cement hydration products.

At the same time, within this report, the following limitations were identified that may influence the interpretation and applicability of the results:

1. Representativeness of experimental conditions

Laboratory tests and numerical simulations were conducted under controlled conditions, which may not fully reflect real conditions and may not take into account all factors present in the host environment;

2. Limiting the time interval

Experimental tests cover relatively short periods of time, which requires extrapolations to estimate very long-term lifetimes (tens or hundreds of years), and this is why errors can occur.

3. Limited use or lack of analysis and measurement equipment

Unforeseen situations may arise regarding the availability and functionality of certain equipment or facilities.

Through the above, the paper demonstrates that cement-based materials, especially those of the CEM II/B-M type, can be optimized for their use in the construction of engineered barriers of the radioactive waste repository, by controlling the hydration process, through microstructural design to achieve strict requirements for durability, mechanical strength and effective chemical barrier. At the same time, the integration of experimental analyses in advanced modeling provides a modern, complete and predictive approach for the use of cement-based materials in critical applications such as their use as the main material in the engineered barrier system.

8.1 Personal contributions

This work represents the result of a complex research activity, in which personal contributions were materialized in several directions, as follows:

- **Elaboration and implementation of experimental determinations and tests**, by designing a series of tests for the physio-chemical and mechanical characterization of the mortar based on composite cement type CEM II/B-M, under different exposure conditions (leaching, carbonation, decalcification).
- **Applying and running thermodynamic and kinetic simulation models** of hydration and degradation processes, using specialized databases and dedicated software tools, including their calibration based on own experimental results.
- **Correlating experimental results with theoretical models**, obtaining predictive relationships between the degree of hydration and mechanical strength, relevant for evaluating the durability of cementitious materials in aggressive environments.
- **Running and interpreting radionuclide sorption tests on mortars**, with direct implications in the field of safe storage of radioactive waste.

8.2 Originality and scientific impact of the thesis

The novelty of this work consists in the integration of an extended and integrated experimental framework with the modeling of hydration and degradation processes of materials based on CEM II/B-M cement, in the context of their use as engineering barriers in environments that simulate processes and conditions specific to radioactive waste repositories, using real information and data, which allowed the creation of aqueous solutions that chemically simulate the deep waters characteristic to the area and geology of the future Saligny waste repository site.

Thus, the results obtained will provide vital information about the evolution of the properties of the materials used in the construction of the engineering barrier system, constituting the technical support in assessing the durability and demonstrating the security function associated with the mortars and concretes used in the construction of the storage cells and the engineering barrier system related to the future surface repository for low and intermediate level waste.

8.3 Continuation Proposals

Based on the results obtained in this thesis, the following research directions are recommended to continue, deepen and expand knowledge in the field of cement-based materials used in engineering barrier systems:

- Continuing studies related to the analysis of solutions that constituted the potential source of mortar degradation, in order to collect data on the effect of the tests carried out on the durability of the investigated materials;
- Continuing permeability studies by completing information and data regarding the impact of degradation on this property;
- Continuation of sorption studies by resuming and continuing studies related to sorption on matrices in which equilibrium was not reached or anomalies were observed, as well as completing them with desorption tests to evaluate the reversibility of sorption of radionuclides studied on cement-based matrices;

- Investigation of degradation processes on the transport of radionuclides by diffusion and on the reinforced concrete structures;
- Investigating the influence of ionizing radiation on the microstructure and mechanical properties of cement-based materials;
- Study of the combined effect of complex interactions between carbonation, leaching and sulfate attack processes in nuclear environments;
- Development of new conditioning matrices that will allow the incorporation of problematic waste such as aluminum waste.

These continuation proposals are based on the requirement for security and integrity of long-term containment and isolation systems for ionizing radiation sources, as well as the desire to contribute to the development of innovative, durable cement-based materials adapted to host environmental conditions.

The work proposed to be continued will largely be carried out in the framework of SUDOKU project work package "Near-surface disposal optimisation based on knowledge and understanding" of the joint European partnership in the field of radioactive waste management (EURAD-2), a partnership co-financed by the European Commission and in which RATEN ICN is a partner.

8.4 List of presented papers

Articles in WOS indexed journals

I. C. Florea, C. M. Bucur, E. A. Florea, C. E. Diaconescu, D. Dupleac „*The effect of curing temperature on the hydration process of CEM II cement type*”, U.P.B Scientific Bulletin Series B, Vol. 87, Issues 1, ISSN 1454-2331, pp. 69-80, 2025;

C. E. Diaconescu, S.D. Dulugeac , A. D. Negrea, **I. C. Florea**, D. Dupleac „*Preliminary Assessment Of The Radionuclides Inventory In Irradiated AlMg₃ Alloy*”, .P.B Scientific Bulletin Series B, Vol. 87, Iss. 1, ISSN 1454-2331, pp. 147-162, 2025;

I. C. Florea, C. M. Bucur, C. E. Diaconescu, E. A. Florea, C. E. Ichim, „*Analysis of the hydration process of CEM II/B-M composite cement*”, Journal of Science and Arts, Vol. 24, Issue 3, ISSN 1844-9581, pp. 735-746, 2024;

C. E. Diaconescu, M. Dianu, C. Bucur, **I. C. Florea**, V. Neculae, „*Studies to Establish the Scaling Factor Methodology for Liquid Radioactive Waste Generated by TRIGA Reactor*”, Journal of Science and Arts Volume 24, Issue 1, pp. 185-198, 2024.

Articles in BDI indexed journals

C.E. Diaconescu, M. Dianu, **I.C. Florea**, „*Influence of Co-60 in Separation, Purification, and Quantification of Ni-63 from Radioactive Waste Samples*”, Journal of Nuclear Research and Development (JNRD), No. 29, pp. 43-47, 2025.

M. Manolescu, C. Bucur, **I. Florea**, S. Lăliu „*Geopolymer-Based Matrices for Conditioning Radioactive Waste*”, Journal of Nuclear Research and Development (JNRD), nr. 26, pp. 24-48, 2024;

C. Bucur, C. Ichim, **I. Florea**, C. Diaconescu, „*Cementitious Materials Characterisation by Inductively Coupled Plasma Emission Spectroscopy*” Journal of Nuclear Research and Development (JNRD), nr. 26, pp. 48-54, 2023;

C. Ichim, C. Bucur, M. Olteacu, **I. Florea** „*Effect of Organics and Cement Degradation on ^{63}Ni Solubility in Cement Pore Waters*”, Journal of Nuclear Research and Development (JNRD), nr. 25, pp. 11-15, 2023;

I. Florea, C. Diaconescu, C. Bucur și A. R. Budu Stănilă, „*Modelling of Cement Hydration using PHREEQC Code*”, Journal of Nuclear Research and Development (JNRD), nr. 24, pp. 33-37, 2022;

C.E. Diaconescu, **I.C. Florea**, C. M. Bucur, și A. R. Budu Stănilă, „*Assessment of Gamma Dose Rate for Waste Packages with Radioactive Concentrate using Microshield Software*” , Journal of Nuclear Research and Development (JNRD), nr.24, pp 38-42, 2022.

International conferences

C. Ichim, C. Bucur, **I. Florea**, D. Dupleac, „*Formate uptake in cementitious systems*”, 6th International Workshop on Mechanisms and Modelling of Waste / Cement Interactions, Prague, 2023;

I. Florea, C. Diaconescu, C. Ichim, I. Prisecaru „*Modelling of Cement Hydration using PHREEQC Code*”, The 14th Annual International Conference on Sustainable Development through Nuclear Research and Education, 2022;

C.E. Diaconescu, **I.C. Florea**, C.M. Bucur, A.R. Budu Stănilă, „*Assessment of Gamma Dose Rate for Waste Packages with Radioactive Concentrate using MICROSHIELD Software*”, The 14th Annual International Conference on Sustainable Development through Nuclear Research and Education, 2022.

C. Diaconescu, M. Mihalache, **I. Florea**, C. Ichim, „*Efficiency Calibration Methods of GeHP Detector for Gamma Ray Measurements from Solid Radioactive Waste*”, The 13th Annual International Conference on Sustainable Development through Nuclear Research and Education, Nuclear 2021;

C. Diaconescu, L. Bujoreanu, **I. Florea**, Ilie Prisecaru, „*Assessment of the Tritium and Gamma Ray Emitters Activities in Liquid Radioactive Waste Generated by TRIGA Reactor*”, 23rd International Conference “New Cryogenic and Isotope Technologies for Energy and Environment” EnergEn 2021, Băile Govora, Romania, October 26 – 29, 2021.

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