10000 years cement – Can hydrated cement last as much as long-lived radionuclides?

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ABSTRACT

This review is focused on the long-term performance of cementitious materials in a repository for radioactive waste. During the last few years, the disposal of disused sealed radioactive sources (DSRS) in a borehole type repository has been studied by many countries. The borehole concept is particularly useful to dispose of spent nuclear fuel and DSRS. In boreholes for DSRS, cementitious materials are intended to be used as structural material, immobilization matrix and as backfill. The understanding of the performance of these materials is essential to ensure the safety of the facilities during their required lifetime, from centuries to many thousands of years, depending on the initial activity and half-life of the waste. This review approaches the behavior of the cement from the hydration and hardening to the long-term processes that can affect its durability. Three main causes of failure of repository-engineered barriers are recognized: a) the formation of a preferential pathway for the migration of the contained radionuclides to the biosphere; b) loss of resistance and cohesion of the structural cementitious material; and c) the increase in the corrosion processes of the metallic components of the structures that affect the overall containment of the facility.

1. Introduction

K. E. Philipose presented a paper entitled *"500 year concrete for a radioactive waste repository"*, in the Waste Management Symposia of 1988 [1]. The paper described the work aimed at *"design(ing) a durable concrete and predict its longevity under the repository environment"*. Almost 30 years after that approach, many issues regarding the hydrated cement durability in the long term are still unresolved and needing more investigation. (see Table 4)

For many years, the Nuclear and Energy Research Institute (IPEN/CNEN-SP) in São Paulo, Brazil, has been developing a borehole concept repository to dispose of disused sealed radioactive sources (DSRS) [2]. In this concept, cement grout is intended to be used between the outer surface of stainless steel borehole casing and the geologic formation. Although it was developed independently, the IPEN concept has many features similar to the one developed under the auspices of the International Atomic Energy Agency (IAEA), the Borehole Disposal of Sealed Radioactive Sources (BOSS) concept designed by the Nuclear Energy Corporation of South Africa [3]. A schematic view of the IPEN/CNEN-SP is presented in Fig. 1.

Boreholes are being considered in some countries to dispose of high-level wastes, e.g. high activity strontium and cesium capsules in the USA [Ref.] or DSRS in Brazil, Ghana and Malaysia [Ref.], mainly because of the lower cost in comparison with alternative disposal concepts and because they present the smallest footprint in the earth surface, a feature that reduces the probability of accidental human intrusion in the disposal facility [4–9].

In all cases, cement grout plays a role as structural material or as an engineered barrier against migration of the disposed of radionuclides.

Of all components of a borehole system, the cement grout is the material with the least predictable behavior in the long term. In the last decades, many authors have been studying the durability of hydrated cement in long term, by studying natural analogs, accelerated tests in laboratory, or mathematical modeling of its behavior under certain circumstances [10–20].

The cement hydrates may be unstable in the long-term because their microstructure and mineralogy may change with time as a consequence of re-crystallization of the cement gel or as a result of chemical reaction with aggregates and substances of the environment. In the environment of a deep repository, the hydrated cement will be exposed to higher
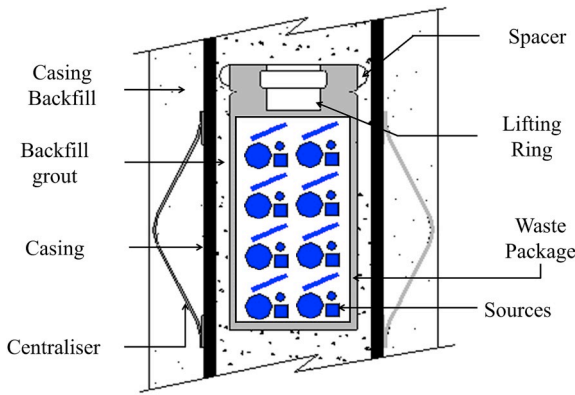
Fig. 1. Borehole concepts to dispose of DSRS developed by IPEN-CNEN/SP.

temperatures and pressures, aggressive chemicals dissolved in the groundwater, and the radiation field of the disposed of waste. These factors are deemed to affect negatively its durability by favoring the changes in the mineralogy and microstructure, thus increasing the porosity and reducing the mechanical resistance [1,10]. The Fig. 2 shows a sketch of the detrimental factors deemed to prevail in a borehole environment and the possible deleterious effects on hardened cement.

This paper aims at reviewing the environmental factors that can affect hydrated cement under a repository environment and at modeling theoretically the long-term behavior of cementitious materials. The following text, at first, presents a review of the mechanisms of action of each individual environmental factors on cement and then discusses possible synergic effects of these factors. This review aims at contributing to the knowledge of the long-term performance of a repository in order to improve the safety assessments of the disposal facility.

2. Literature review – how the environment affects cement durability?

The factors that determine the fate of the cementitious barriers in a repository are the initial, chemical and mineralogical composition of the material and the physical and chemical components of the neighborhood that can change that composition. The normal anhydrous compounds of the cement raw material, the amount of water added and other ingredients like fine and coarse aggregates, and chemical additives to the mixture define the initial composition. The temperature and pressure at the depth of the repository, the dissolved chemicals in any groundwater in contact with the repository structures, and the radiation field generated by the disposed of waste are the physical and

chemical components of the environment that can affect the long-term cement performance.

The discussions about this factors found in the literature are summarized below.

2.1. The hydration and natural evolution of hydrated cement

The water added to anhydrous cement starts the hydration process and the numerous chemical reactions and physical changes that follow. The complexity of the hydration process is due to the high number of components involved, the variability of the composition of different types of cement, and the strong influence of external factors during the hydration [21,22].
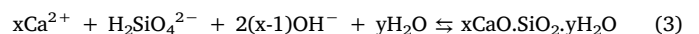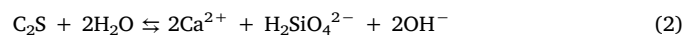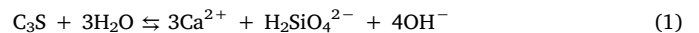
In cement chemistry, the composition of anhydrous and hydrated cement is expressed as abbreviations of the oxide's formulae. The cement notation is used to simplify and shorten the compound formulas as follows:

$C = CaO$; $S = SiO_2$; $A = Al_2O_3$; $F = Fe_2O_3$; $M = MgO$; $\bar{S} = SO_3$; $\bar{C} = CO_2$; $H = H_2O$.
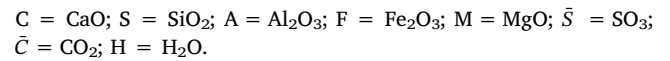
The cement industry also uses the mineral name to identify the compounds involved in cement phases. Table 1 shows the main phases in the cement clínquer (alite, belite, aluminate, and ferrite) and the chemical compounds (gypsum and lime) added to form the anhydrous ordinary Portland cement (OPC). Besides these, a cement clínquer can contain other compounds, like alkaline sulfates and magnesium oxide [23,24].

The anhydrous phases of OPC react with water to form the hydrated products. Hydration in cement is related to a process of dissolution and precipitation, where the anhydrous phase first undergoes dissolution and then the hydrated phases precipitate [25–30]. The main phases formed during the cement hydration are summarized in Table 2.

The C–S–H gel is the first compound formed during the hydration, as result of C_3S and C_2S dissolution and reaction with water. The abbreviation is hyphenated because the stoichiometry of the compound is undefined. Its calcium/silica ratio (C/S) usually varies from 1.5 to 2 in OPC. The dissolution reactions and the C–S–H formation are represented in equations (1)–(3) [22,26,28,30].

$$C_3S + 3H_2O \leftrightarrows 3Ca^{2+} + H_2SiO_4^{2-} + 4OH^- \tag{1}$$

$$C_2S + 2H_2O \leftrightarrows 2Ca^{2+} + H_2SiO_4^{2-} + 2OH^- \tag{2}$$

$$xCa^{2+} + H_2SiO_4^{2-} + 2(x-1)OH^- + yH_2O \leftrightarrows xCaO.SiO_2.yH_2O \tag{3}$$

The C/S ratio depends on the calcium ions in the solution. These ions are released from the dissolution of lime (equation (4)), C_3S and C_2S, but also react to form Portlandite (equation (5)), that is another important hydration product [22].
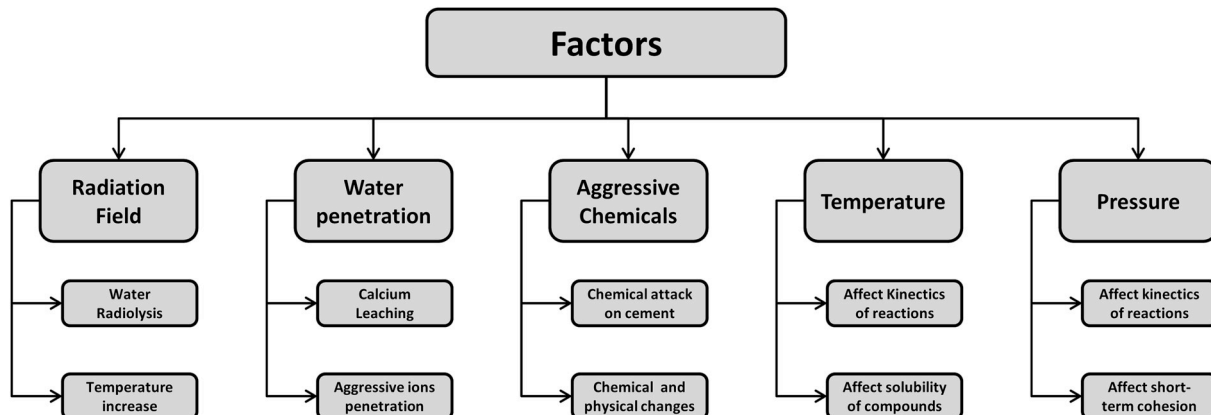

Fig. 2. Environmental factors and their possible deleterious effects on hardened cement.

Table 1

Mineralogical composition of anhydrous Portland cement.

Chemical Name	Mineral Name	Cement Notation	Chemical formula	Weight %
Tricalcium silicate	Alite	C_3S	$3CaO \cdot SiO_2$	60–65
Dicalcium silicate	Belite	C_2S	$2CaO \cdot SiO_2$	10–20
Tricalcium aluminate	Aluminate	C_3A	$3CaO \cdot Al_2O_3$	8–12
Tetracalcium aluminoferrite	Ferrite	C_4AF	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	8–10
Calcium sulfate dihydrate	Gypsum	$C\check{S}H_2$	$CaSO_4.2H_2O$	–
Calcium Oxide	Lime	C	CaO	–

Table 2

Compound of hydrated portland cement.

Chemical Name	Mineral Name	Cement Notation	Chemical formula
Calcium hydroxide	Portlandite	CH	$Ca(OH)_2$
Calcium silicate hydrate	–	C–S–H	$xCaO \cdot SiO_2 \cdot yH_2O$
Calcium trisulfoaluminate hydrate	Ettringite or AFt	$C_6A\check{S}_3H_{32}$	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$
Calcium Monosulfate[a]	AFm	$C_4A\check{S}H_{12}$	$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$
		$C_4A\check{S}H_{18}$	$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 18H_2O$
Calcium Monocarbonate[a]	AFm	$C_4A\bar{C}H_{11}$	$3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$
Calcium Aluminate[a]	Hydrogarnet	C_3AH_6	$3CaO \cdot Al_2O_3 \cdot 6H_2O$

[a] These compounds represent the main minerals of AFm, Hydrogarnet and Ettringite phases, which have a range of compositions that can be formed during cement hydration at different conditions.

Table 3

Legend of the effects of each factor identified in the conceptual map.

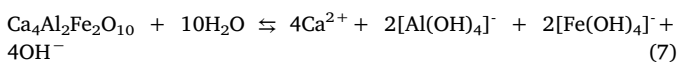| ID	Description
A1	**C–S–H crystallization and chain polymerization.** C–S–H crystallization and polymerization occur naturally in the cement in long-term. It leads to a lower Ca/Si ratio and to C–S–H decalcification.
A2	**Loss of water in long-term and decrease in relative humidity.** The water loss in long term occurs in cementitious materials as the hydration process slowly continues during many years after the cure. With water loss, the relative humidity decrease and leads to autogenous shrinkage.
A3	**Alkali-Aggregate reactions (AAR).** The most common AAR is the alkali-silica reaction (ASR). The other form is the alkali-carbonate reaction (ACR). It changes the chemical composition of cement causing cracking in the cement-aggregate interface and expansion. It forms a preferential pathway for water ingress in the material.
B1	**Water Radiolysis.** Radiolysis is the chemical decomposition of the water that creates reactive chemical species and radicals, by interaction of radiation with matter. This process causes Portlandite consumption and water loss due to gas formation.
B2	**Irradiation effects on temperature increase.** The absorption of the radiation energy inside a material causes internal heating and increase in the temperature. The increase rate and the total increase in temperature depend on the type of radiation, the activity of the radioactive source and the total accumulated dose.
B3	**Irradiation effects on pressure increase.** The water decomposition generates gases as H_2 and O_2 that accumulate in the cement pores, increasing the pressure exerted in the cement.
C1	**Solubility changes in cement phases.** The solubility of the cement compounds is affected by the temperature increase and has a significant impact in the C–S–H phase. Increasing temperature leads to compounds with lower Ca/Si ratio and to a higher calcium concentration in the pore water.
C2	**Chemical decomposition of cement phases.** The chemical decomposition of some compounds of hydrated cement in high temperatures (above 100 °C for the C–S–H, between 450 and 500 °C for the Portlandite and 700-900 °C for the calcite). Changes in the compound structures occur at lower temperatures, like ettringite and C–S–H at 50 °C.
C3	**Water loss due to drying.** Between 30 and 120 °C the free and combined water is lost by drying. This process leads to a lower relative humidity and causes shrinkage.
C4	**Changes in the kinetics of chemical reactions.** The kinetics of chemical reactions are affected due to temperature variation. During hydration, these changes lead to a higher hydration rate but lower final hydration degree. Other chemical reactions are promoted by the change in reaction kinetics, as DEF.
C5	**Temperature effects on pressure increase.** The water evaporation caused by temperature increase leads to an increase in the internal pressure in the cement.
D1	**Densification of the material.** The pressure leads to a densification and causes water loss, decreasing the space available for water, increasing the relative humidity. It leads to chemical shrinkage and changes in the C–S–H layers.
D2	**Changes in the kinetics of chemical reactions.** The kinetics of chemical reactions are changed by increasing pressure, like carbonation and higher hydration rate and lower setting time during hydration.
E1	**Leaching of cement compounds.** Leaching of cement compounds leads to depletion of Portlandite and decalcification of C–S–H, and decreasing of pore water pH.
E2	**Penetration of aggressive ions.** Groundwater penetration in the cement may carry aggressive dissolved ions that react with the material, leading to deleterious chemical reactions inside the cement.
F1	**Chemical reactions with cement phases.** Ions that penetrate the cement and react with hydrated phases cause loss of calcium, depletion of Portlandite, and decalcification of C–S–H, changing cement mineralogical composition. Sulfate penetration leads to the formation of ettringite, gipsite and thaumasite and causes expansion and cracking. Chloride penetration increases significantly the corrosion rate and changes cement porosity. Reaction of carbonate with calcium forms calcite what leads to changes in cement porosity and permeability. Magnesium penetration causes formation of brucite and a M-S-H phase, decreasing the pH and increasing cement porosity.
F2	**Adsorption on the cement phases.** Some ions penetrate the cement and can be absorbed in the hydrated compounds, especially in the C–S–H interlayer. Chloride and carbonate can be adsorbed in the positive layers of the C–S–H and exchanged with hydroxyl, releasing this ion to the solution. Exchange of calcium by cations of magnesium and sodium leads to a weakening of the cement matrix and the release of calcium ions.
F3	**Penetration of free ions in the material.** Some ions that penetrate cement paste, especially if in higher concentrations, change the pore water composition and increase corrosion of metallic structure components. Chloride and carbonate are the most important ions that increase the corrosion of metals.

$$CaO + H_2O \leftrightarrows Ca^{2+} + 2OH^- \qquad (4)$$

$$Ca^{2+} + 2OH^- \leftrightarrows Ca(OH)_2 \qquad (5)$$

The C_3A hydration occurs very quickly under regular conditions. To slow down the reaction and improve cement workability, gypsum is added to the cement clinker.

The C_3A and C_4AF dissolution lead to the formation of AFt and AFm phases. The dissolution of C_3A and C_4AF are represented in equations (6) and (7), respectively.

Table 4
Legend of the connectors of the conceptual map.

ID	Description
1	Loss of water in the long-term, reduce relative humidity (R.H.).
2	Loss of water by decomposition caused by radiolysis
3	Loss of water by drying at high temperatures
4	Loss of water by densification. High pressure can increase R.H.
5	Alkali-Aggregate reactions – changes in the cement composition.
6	Water radiolysis generates gas and reactive radicals. Increase in carbonation process.
7	Chemical decomposition at high temperatures (above 100 °C).
8	Lower hydration degree in the long term. Favors deleterious reactions, as DEF.
9	Microstructural changes by C–S–H densification.
10	Lower hydration degree in the long term. Favors carbonation reactions
11	Leaching and calcium loss. Formation of phases as brucite and M-S-H.
12	Penetration of ions and reactions with cement hydration compounds.
13	Portlandite depletion during radiolysis. Formation of calcium compounds.
14	Portlandite decomposition at 500 °C. Changes in other cement phases.
15	Loss of calcium from Portlandite. Reduces pH of the pore water.
16	Reactions that consume Portlandite. Sulfate, chloride and magnesium attack.
17	C–S–H crystallization. Changes in the Ca/Si ratio.
18	Solubility changes of crystalline phases. Loss of calcium.
19	Shrinkage due to water loss at C–S–H layers. Changes in the Ca/Si ratio.
20	Reduction of calcium in pore water. Changes in the Ca/Si ratio of C–S–H.
21	Calcium substitution in C–S–H. Decalcification.
22	Loss of water. Lead to shrinkage and cracking.
23	Changes in the cement phases. Loss of resistance and cohesion, cracking and porosity changes
24	Loss of Portlandite. Reduces pH and changes porosity and pore forms.
25	C–S–H decalcification. Reduce pH and changes porosity and pore forms.
26	Chloride and carbonate penetration increases the corrosion of metallic structures.
27	Changes in cement phases by reaction with Portlandite and decalcification of C–S–H. Formation of ettringite, calcite, and brucite, among others.
28	Shrinkage due to loss of water
29	Loss of water leads to cracking
30	Changes in cement phases leading to volumetric changes and cracking.
31	Changes in cement phases leading to volumetric changes and cracking.
32	Loss of calcium from Portlandite and changes in the porosity due to the formation of expansive products.
33	C–S–H decalcification leading to changes in the porosity due to the formation of expansive products.
34	Decrease of pH of pore water by loss of calcium and hydroxide ions.
35	Decrease of pH of pore water by loss of calcium and hydroxide ions.
36	Shrinkage of cement causes detachment of the material and leads to the formation of a preferential pathway between cement and geological setting or steel casing.
37	Cracking leads to the formation preferential pathway
38	Cracking leads to deterioration of the material. Loss of resistance and cohesion.
39	Changes at cement phases lead to loss of resistance and cohesion by the formation of non-cementitious phases (as M-S-H).
40	Widening of pore size distribution and porosity lead to loss of resistance and cohesion.
41	Widening of pore size distribution and porosity lead to a higher penetration of aggressive ions, increasing corrosion of metallic structures.
42	Reduction of pH in pore water reduces the passivation layer provided by cement what increases the corrosion of metallic structures.

$$Ca_3Al_2O_6 + 6H_2O \leftrightarrows 3Ca^{2+} + 2[Al(OH)_4]^- + 4OH^- \tag{6}$$

$$Ca_4Al_2Fe_2O_{10} + 10H_2O \leftrightarrows 4Ca^{2+} + 2[Al(OH)_4]^- + 2[Fe(OH)_4]^- + 4OH^- \tag{7}$$

In the presence of gypsum, ettringite ($C_6A_3H_{32}$) is the first mineral to precipitate in the solution. Other AFt phases can be formed by substitution of sulfate by carbonate and chloride ions, leading to the formation of ettringite-analog phases [31]. After the consumption of all gypsum, the AFm phases start to precipitate with the formation of calcium monosulfate (C_4AH_{12} and $C_4A\bar{S}H_{18}$). The formation of ettringite and monosulfate is represented in equations (8)–(10), respectively.
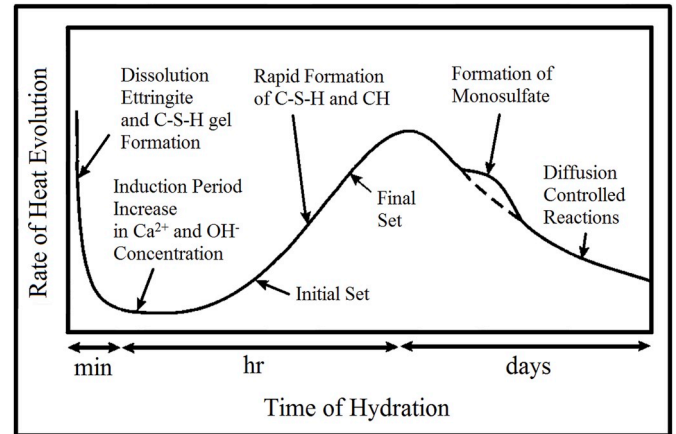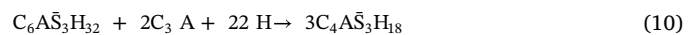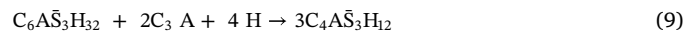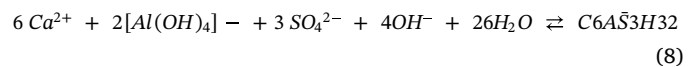
Fig. 3. Schematic representation of heat evolution in cement hydration [32].

$$6\,Ca^{2+} + 2[Al(OH)_4]^- + 3\,SO_4^{2-} + 4OH^- + 26H_2O \rightleftarrows C6A\bar{S}3H32 \tag{8}$$

$$C_6A\bar{S}_3H_{32} + 2C_3A + 4H \rightarrow 3C_4A\bar{S}_3H_{12} \tag{9}$$

$$C_6A\bar{S}_3H_{32} + 2C_3A + 22H \rightarrow 3C_4A\bar{S}_3H_{18} \tag{10}$$

Other AFm common phases are formed during C_3A hydration, without sulfate in its composition, as C_2AH_8 and C_4AH_{19}. In some aluminate cements, the hydrogarnet is the main phase formed during hydration [24,26,32]. The formation of the free-sulfate AFm phases and hydrogarnet is represented in equations (11) and (12).

$$2C_3A + 27H \leftrightarrows C_2AH_8 + C_4AH_{19} \tag{11}$$

$$C_2AH_8 + C_4AH_{19} \leftrightarrows 2C_3AH_6 + 15H \tag{12}$$
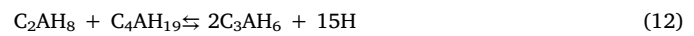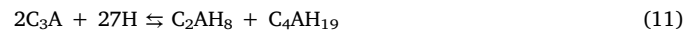
There are many other AFm-type compounds that can be formed, depending on the environmental conditions during the cure of the cement and even after the cure. In a low humidity environment, the C_4AH_{19} monosulfate loses its water and C_4AH_{13} is formed. The sulfate ion can be replaced by any double charged ion, like carbonate that forms the monocarbonates ($Ca_3Al_2O_6.CaCO_3.11H_2O$ and $C_4A\bar{C}H_{11}$), or single charged ions, like chloride ions that forms the Friedel's salt ($Ca_3Al_2O_6.CaCl_2.10H_2O$) [21,33,34].

The rate of heat evolution of an ordinary Portland cement presented by Michaux et al. (1990) is shown in Fig. 3. Two reactions are responsible for the heat production during cement hydration: a) the precipitation of ettringite and b) the formation of C–S–H and Portlandite.

Fig. 3 shows the five periods in the cement hydration process and the heat evolution of each one. The first period is an initial reaction period, characterized by the rapid dissolution of anhydrous compounds and by the formation of ettringite and C–S–H. Secondly, an induction period is observed, where the heat production is lower and an increase in ion concentration in the solution occurs. After this period, in the so called acceleration period, there is another peak of the heat, characterized by the formation of hydrated products, followed by a reduction in the heat production and a slower formation of the reaction products, the so called deceleration period. In an ordinary cement, 50% of the heat is released during the first three days of hydration and 70% during the first 7 days [22,32,35–37].

The hydrated cement paste is a heterogeneous material and has, in its structure, solid materials (hydrated compounds and anhydrous grains), voids (incorporated air and pores) and water (chemically bound or free water) [22].

The C–S–H gel occupies 50–60% of total volume of solids in the hydrated cement paste. Its layered structure has high superficial area and water incorporated between the layers. The Portlandite occupy around 20–25% of the volume, while the AFm and AFt phases around
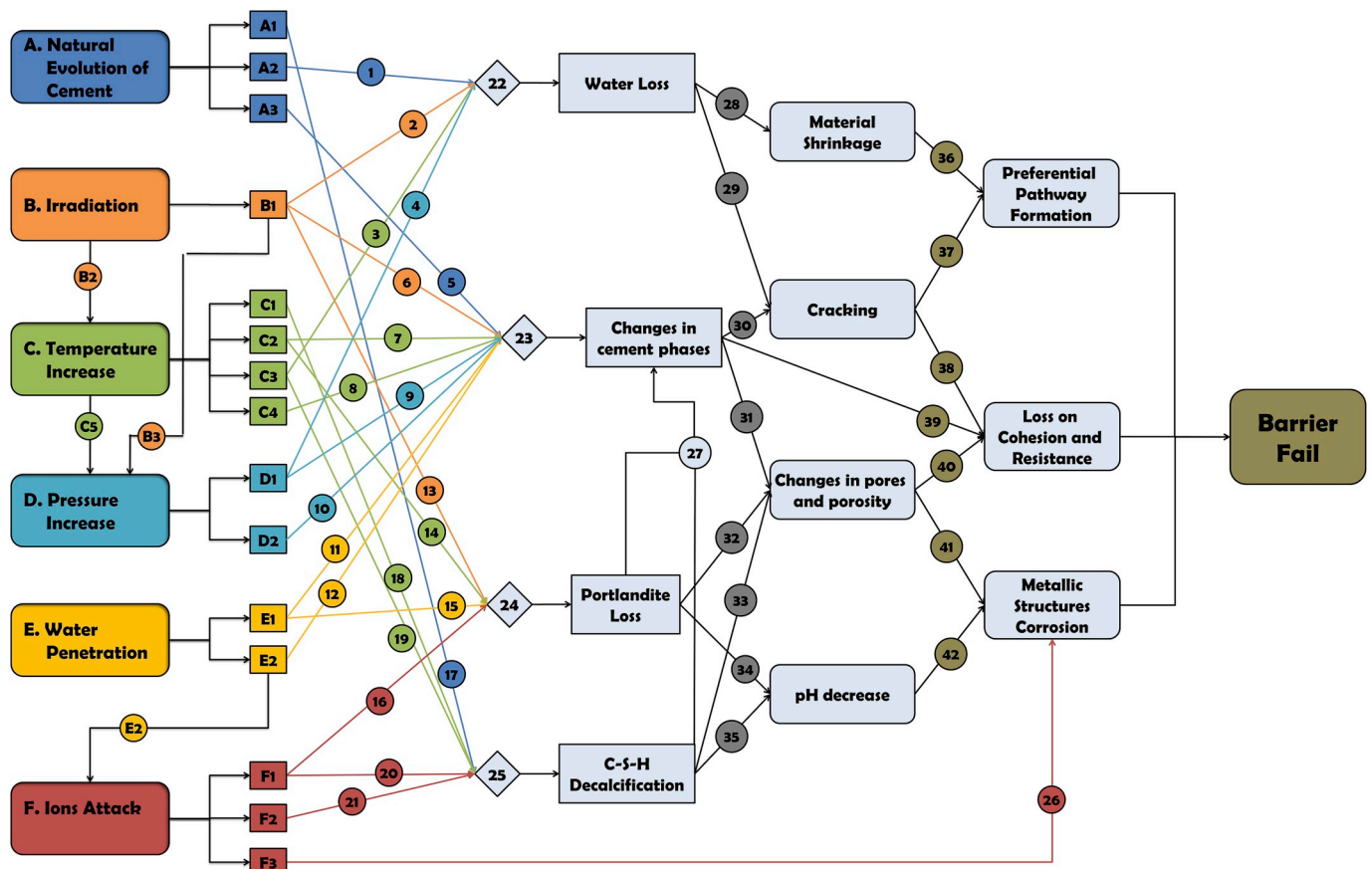
Fig. 4. Overview of the conceptual map of cement long-term durability.

15–20%. At early ages, ettringite is the main component of the sulfoaluminate phases, but as the hydration progresses, it transforms into monosulfate [22,24].

The voids in cement paste is a combination of interlayer space in the C–S–H, capillary voids and air voids. The space between C–S–H layers can be also filled with water. The capillary voids depend upon the water/cement ratio of the mixture and the hydration rate. Air voids are formed during the hydration by the air trapped in the paste during mixing [22,26,38].

The hydrated cement paste is capable of retaining a large amount of water, which can be retained in the capillary pores, physically adsorbed on the solids surface, locked in the interlayer space of the C–S–H structure and chemically bound in the hydrated compounds [22].

The free water in the large capillary pores (voids of the order of > 50 nm) can be easily removed from the structure without significant changes in the volume. However, the watercan be retained in small voids (5–50 nm) and be held by capillary tensions, causing shrinkage in the cement paste when removed [22].

Chemically bound water is integrated within the molecules of hydration products and can only be removed by chemical decomposition of these compounds. The water in the C–S–H interlayer space was investigated by many authors in the last years [30,39–41], who reported that this water is physically adsorbed among C–S–H particles [39], or chemically adsorbed in the C–S–H structure [30,36,41], or trapped in the layers [40].

The water and air content of the hydrated cement paste is strongly dependent on the recipe of the mixture, especially the water/cement (w/c) ratio. A higher w/c ratio and air content result in a higher free water content, higher porosity of the material and lower mechanical strength [34,42].

Cementitious materials cured in high temperatures are common in

precast products in the modern concrete industry. When exposed to high temperatures during cure, the hydration rate and the development of mechanical strength are accelerated. However, in the long term, the final degree of hydration and the mechanical strength are lower. High-temperature cure causes micro cracks, shrinkage and need a higher w/c ratio [43–50].

Water content, porosity (amounts of air voids in the material), and mechanical strength are some of the properties of hydrated cement materials that affect its long-term performance. The dimensional stability of the hardened material is another one. The shrinkage is an intrinsic characteristic of the cementitious material and occurs when the material loses some of the water inside it. The effects of chemical shrinkage are higher when the material is exposed to higher temperatures and environment with low relative humidity.

Alkali-aggregate reactions (AAR) are a well-known cause of cement damage that happen in mortars and concrete. These reactions occur between hydroxyl ions associated to alkalis in the cement and reactive compounds from aggregate materials. AAR occurs in the presence of water and high amounts of alkalis in cement porewater. The aggregate size also influences the effects of AAR, since the larger particles induces a larger reaction The AAR is an expansive reaction that leads to an increase in porosity and cracking [21,34,55–58].

Many works addressed the long-term performance of cementitious materials and deformation processes, as drying and autogenous shrinkage and creep [59–72]. It must be pointed out that long-term performance, in the case of radioactive waste repositories, differs significantly from the long-term performance required from the usual engineering structures, for which the required lifetime is of hundreds of years, at maximum.

In their paper of 2017, Rahimi-Aghdam et al. [72] addressed the hydration evolution of cement in a timeframe of centuries. They
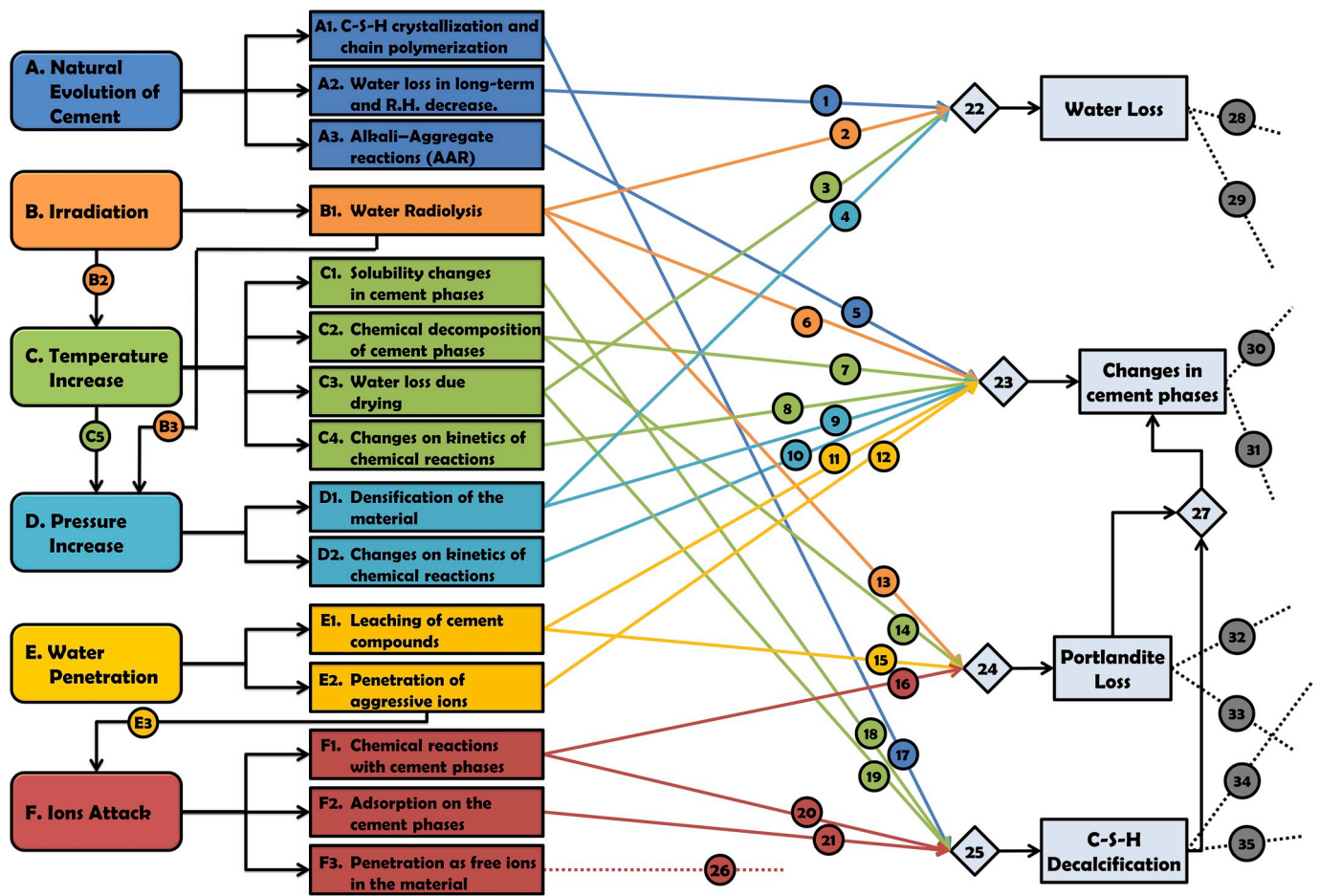
Fig. 5. Details of primary effects of the conceptual map of cement long-term durability.

proposed that the anhydrous grains that remain in the material are involved by the hydrated compounds that maintain the grains intact for years. A long-term hydration process then takes place by the slow penetration of water through the C–S–H shells to reach these grains. The hydration of these remaining grains leads to the autogenous shrinkage of the cement paste and the formation of microcracks, increasing cement permeability and decreasing resistance to chemical attack.

Creep and shrinkage of the cementitious materials were reported to increase linearly with time, w/c ratio and with the content of aggregates. It was also noted that the increase in the diameter of the fine aggregates can decrease creeping.
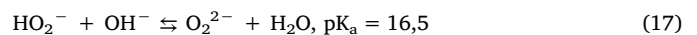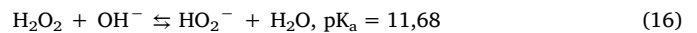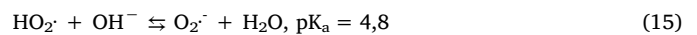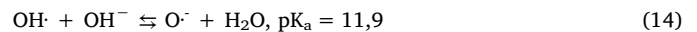
2.2. The effects of a radiation field

In a borehole-type repository for DSRS, the gamma radiation field created by the sources can affect cement mineralogy. The problems associated with the radiation in the cement are the changes caused by the interaction of the radiations with the electrons of the chemical bonds that results in radiolysis, mainly of water, and temperature increase in the material. The expected accumulated radiation dose absorbed by cement until the decay of the disposed of radionuclides is in the order of megagrays. In the cement compounds themselves, these doses are insufficient to change the mineral composition, but the products of the radiolysis of water will certainly do [73–75].

Radiolysis of water is a process that breaks the chemical bonds of water and can cause water loss in the cement matrix. This phenomenon, in synergy with temperature increase, changes cement microstructure and cause creep and dry shrinkage of cement matrix. Since the effects of radiation in the cement are directly dependent on temperature, the
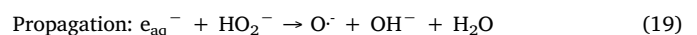
synergetic effects of both process have to be taken into account [76,77].

The cement paste and the aggregates in mortar, grout or concrete behave differently when exposed to radiation. While the cement paste shows shrinkage due to water loss, the aggregates usually show expansion due to changes in its crystalline structure. The radiation causes an increase in alkali-aggregate reactions, that are highly deleterious to the material because cause its expansion [76,78].

The radiolysis of water generates many compounds, as $H_{2(g)}$, H_2O_2, OH^- and H_3O^+ and chemical radicals as e_{aq}^-, $H\cdot$, $OH\cdot$, $HO_2\cdot$ [79]. A radiation rate of about 10^{-3} to 10^{-5} Gy/s is able to impact significantly the cementitious materials by radiolysis that began almost immediately after the radiation reaches the cementitious material [73]. Secondarily, the radiolysis products react with hydroxyl ions to re-form water and other radicals, as shown in equations (13)–(17) [79]:

$$H\cdot + OH^- \leftrightarrows e_{aq}^-, pK_a = 9,6 \tag{13}$$

$$OH\cdot + OH^- \leftrightarrows O\cdot^- + H_2O, pK_a = 11,9 \tag{14}$$

$$HO_2\cdot + OH^- \leftrightarrows O_2\cdot^- + H_2O, pK_a = 4,8 \tag{15}$$

$$H_2O_2 + OH^- \leftrightarrows HO_2^- + H_2O, pK_a = 11,68 \tag{16}$$

$$HO_2^- + OH^- \leftrightarrows O_2^{2-} + H_2O, pK_a = 16,5 \tag{17}$$

The formed new species are mostly more reactive than the primary products. In an alkaline environment like the cement pore water, the chain reaction that controls the primary products and water re-formation is presented in equations (18)–(20) [79].:
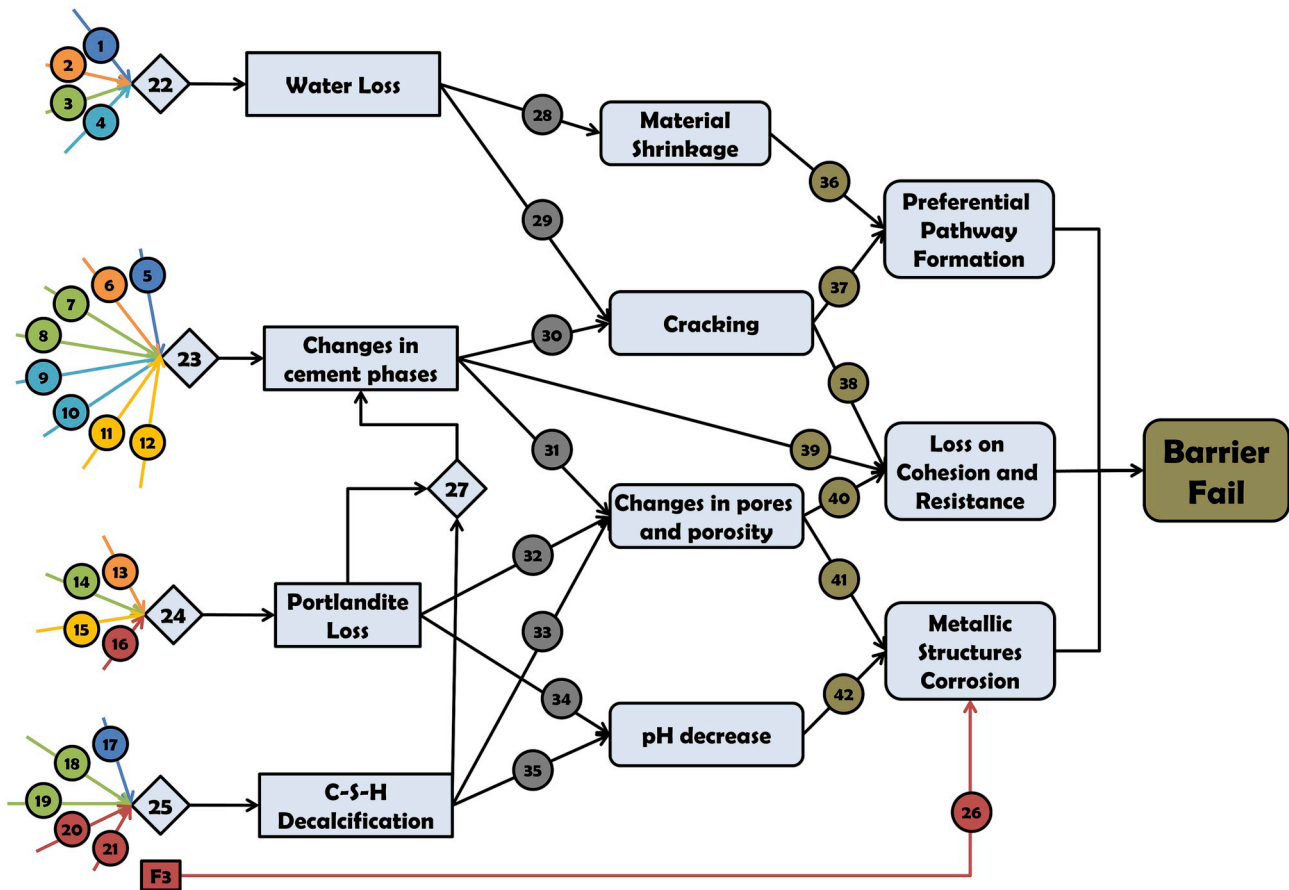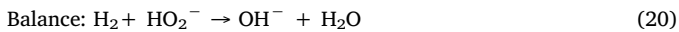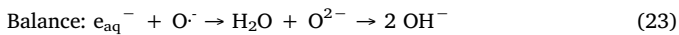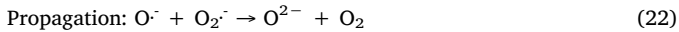
$$\text{Initiation:} O\cdot^- + H_2 \rightarrow e_{aq}^- \tag{18}$$

$$\text{Propagation: } e_{aq}^- + HO_2^- \rightarrow O\cdot^- + OH^- + H_2O \tag{19}$$
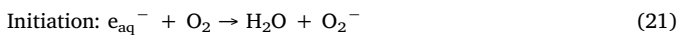
Fig. 6. Details of secondary effects of the conceptual map of cement long-term durability.

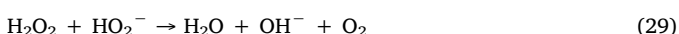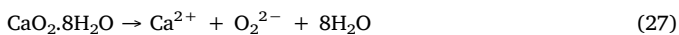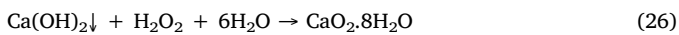Balance: $H_2 + HO_2^- \rightarrow OH^- + H_2O$ (20)

This chain reaction is able to destroy the H_2 formed during radiolysis but, after a while, the O_2 formed start to accumulate and an alternative chain initiate. This chain is presented in equations (21)–(23) [79,80]:

Initiation: $e_{aq}^- + O_2 \rightarrow H_2O + O_2^-$ (21)

Propagation: $O^{\cdot} + O_2^{\cdot-} \rightarrow O^{2-} + O_2$ (22)

Balance: $e_{aq}^- + O^{\cdot} \rightarrow H_2O + O^{2-} \rightarrow 2\,OH^-$ (23)

The radiolysis products react with themselves and form oxygen gas. The reactions shown in equations (24) and (25) are the reactions that prevail in the alkaline environment [79]:

$H_2O_2 + O_2^{\cdot-} \rightarrow O_2 + OH^{\cdot} + OH^{\cdot}$ (24)

$HO_2^- + O_2^{\cdot-} \rightarrow O_2 + O^{\cdot} + OH^-$ (25)
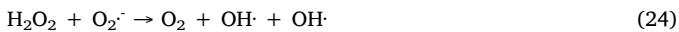
The formed chemical compounds and radicals can also interact with hydrated cement compounds. The reaction between Portlandite and hydrogen peroxide was reported years ago by Bouniol and Aspart (1998) indicating a formation of calcium peroxide octahydrate [81]. This chain reaction is represented by equations (26)–(31).

$Ca(OH)_2\downarrow + H_2O_2 + 6H_2O \rightarrow CaO_2.8H_2O$ (26)

$CaO_2.8H_2O \rightarrow Ca^{2+} + O_2^{2-} + 8H_2O$ (27)

$O_2^{2-} + H_2O \rightarrow HO_2^- + OH^-$ (28)

$H_2O_2 + HO_2^- \rightarrow H_2O + OH^- + O_2$ (29)

$Ca^{2+} + 2\,OH^- \rightarrow Ca(OH)_2\downarrow$ (30)

Balance: $2H_2O_2 \rightarrow 2H_2O + O_2$ (31)

The formation of calcium peroxide stores the oxygen during the radiolysis, while the H_2O_2 is being generated. In closed systems, this mechanism regulates the system and the effects of radiolysis in the material are limited [38,79,82].

Many investigations during the first years of nuclear era addressed the effects of radiation on cementitious materials. However, between 1980 and 2005, there was a gap in this area. After 2005, the lifetime of many nuclear installations was extended and, as consequence, also the lifetime of cementitious materials [83–85].

One of the first works published on the effects of radiation on cementitious materials was that of Sommers, in 1969, who exposed cement specimens to a maximum gamma dose of 10^9 Gy. The results presented by Sommers showed that irradiated samples had a mechanical strength about 30% lower than control samples. Also, the leaching of on irradiated samples was higher [86].

Progressive damage in cementitious specimens exposed to gamma radiation field was reported by many others since then. The dose threshold, however, is not yet a consensus. In general, irradiation causes changes in the cement microstructure and a lowering in mechanical strength. These changes in cement structure were strongly dependent on dose rate and total dose, as well as on the temperature increase due to irradiation [86–94].

Neutron irradiation of cementitious specimens also showed that the damage in the material was dependent on the total dose and dose rate [95–99].

2.3. The effects or water penetration

Water penetration into the cementitious matrix leads to leaching of

chemical species from the hydrated cement and to the penetration of minerals, salts, metals, cations or anions dissolved in the water into the matrix (see section 2.4). Calcium leaching as well the penetration of aggressive chemicals is the major problems associated with the water penetration in the cement.

The leaching of calcium leads to the loss of Portlandite content and to the decalcification of C–S–H, what can affect the cement durability in up to 50% [1]. Other factors that can affect the process are the ground water flow rate, the initial porosity of the hydrated cement, and the temperature [100,101].

Calcium leaching leads to an increase in porosity and a decrease in the pH of the pore water. Decalcification of C–S–H gel generates a low calcium/silica ratio in this phase and the poisoning with magnesium and chloride ions, that substitute the calcium in the C–S–H gel [102,103].

2.4. The effects of penetration of ions of aggressive chemicals
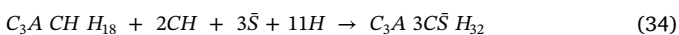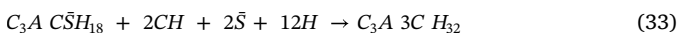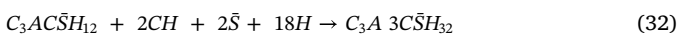
2.4.1. Sulfate attack

Among the phenomena that lead to cement degradation, the sulfate attack is the most studied and known. Sulfates are present in different environments and their penetration in cement paste is a risk to the performance of structures made of cementitious materials.

The reaction of sulfate with hydrated products can lead to the formation of gypsum, ettringite, and thaumasite causing fissures, cracking and expansion with the consequent loss of strength and other damages to cement materials. Physical and chemical factors as pH values, sulfate concentration, the associated cation, w/c ratio and cure condition of the material are some factors that can influence the occurrence and the intensity of the attack [104,105].

The gypsum formation causes a reduction in the pH value and loss of mechanical strength. The ettringite formation after the cement setting is an expansive reaction and is the main cause of damage in the material when sulfate react with the material [105].

The sulfate can be provided by external or internal sources. External sulfate penetrates and damages the cement material when three conditions are present: a) high permeability of the material; b) sulfate-rich environment; and c) presence of water. The associated cation plays an important role in the sulfate attack. Calcium and magnesium cations are the most reactive and form insoluble phases, changing the cement mineralogy [104–106].

Two distinct periods are observed in the sulfate attack. First, a dormant period that can last for years, during which expansion is not observed, followed by the second in which the porosity increases and an expansion of the material occurs. The reaction with external sulfate contributes for Portlandite depletion and C–S–H decalcification [34,104,107]. The reactions of sulfate with some AFm phases to form ettringite are represented in equations (32)–(34). It is possible to observe the Portlandite depletion and the water dependence of these reactions, as both are reactants.

$$C_3A C\bar{S} H_{12} \ + \ 2CH \ + \ 2\bar{S} \ + \ 18H \rightarrow C_3A \ 3C\bar{S}H_{32} \tag{32}$$

$$C_3A \ C\bar{S} H_{18} \ + \ 2CH \ + \ 2\bar{S} \ + \ 12H \ \rightarrow C_3A \ 3C \ H_{32} \tag{33}$$

$$C_3A \ CH \ H_{18} \ + \ 2CH \ + \ 3\bar{S} \ + \ 11H \ \rightarrow \ C_3A \ 3C\bar{S} \ H_{32} \tag{34}$$

Gypsum formation is an ion exchange reaction, in which the external sulfate replaces the hydroxyl ions of the Portlandite. The reaction of sodium and magnesium sulfate with Portlandite are represented in equations (35) and (36), respectively. The magnesium is more aggressive than sodium, since the magnesium hydroxide precipitates and reduces drastically the pH of the pore solution (see section 2.4.4) [22,106].

$$Na_2SO_4 \ + \ Ca(OH)_2 \ + \ 2H_2O \rightarrow CaSO_4.2H_2O \ + \ 2NaOH \tag{35}$$

$$MgSO_4 \ + \ Ca(OH)_2 \ + \ 2H_2O \rightarrow CaSO_4.2H_2O \ + \ Mg(OH)_2 \tag{36}$$

If sulfate is provided by internal sources, the process is called Delayed Ettringite Formation (DEF). DEF occurs when there are excess of sulfate in the matrix, elevated temperatures and presence of water [108–110].

Many researchers reported that DEF only occurs in materials that have been cured in high temperatures. However, some cases of DEF occurrence are found in materials that were not submitted to high-temperature cure [111]. In fact, higher cure temperatures lead to an increase in micro-cracking, which is necessary to the ettringite deposition in the hardened matrix [105].

The sulfate in DEF can be provided by the presence of gypsum, contamination on aggregates, decomposition of hydrated products, as ettringite, or by the slow release of adsorbed sulfate ions from C–S–H [105,112].
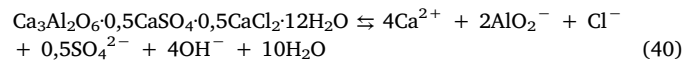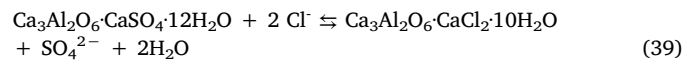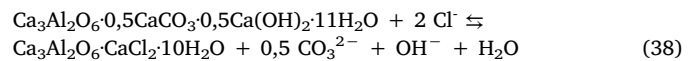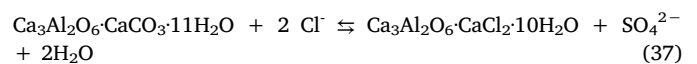
2.4.2. Chloride attack

Chloride attack is the main cause of corrosion of steel bars in concrete. In the waste repository, it can lead to corrosion of borehole steel casing and waste containers. Chloride penetration in cementitious materials can lead to damage and even the collapse of the structure due to changes in physical, chemical and mechanical properties of the material [113–115].

The chloride that penetrates into the cement can be in three distinct forms: 1) chemically bound in AFm phases of hydrated cement, b) adsorbed on C–S–H layers, or c) as free ions in the pore solution. The free ions penetrate the cement matrix and if reach the steel bar, they lead to a corrosion process [116,117].
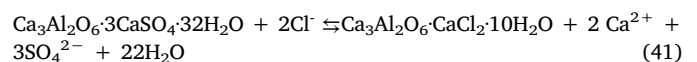
If chlorides are chemically bound, it forms salts as Kuzel's and Friedel's salts ($C_3A.0.5CaCl_2.0.5CaSO_4.H_{12}$ and $C_3A.CaCl_2.H_{10}$). Another compound commonly found in the cement matrix is the calcium oxychloride, which can cause expansion and cracks in the cementitious matrix [113–115,118,119].

The nature and extension of chloride penetration, reaction, and damage in a cementitious material depends upon factors, as temperature, chloride concentration, pH value of the environment and chloride-associated cation [115,120].

Chloride reaction with monosulfate, hemicarbonate and monocarbonate to form Friedel's salt are represented in equations (37)–(39), respectively. The Kuzel's salt formation and dissolution are represented in equation (40).

$$Ca_3Al_2O_6 \cdot CaCO_3 \cdot 11H_2O \ + \ 2 \ Cl^- \ \leftrightarrows \ Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O \ + \ SO_4^{2-} \ + \ 2H_2O \tag{37}$$

$$Ca_3Al_2O_6 \cdot 0,5CaCO_3 \cdot 0,5Ca(OH)_2 \cdot 11H_2O \ + \ 2 \ Cl^- \ \leftrightarrows$$
$$Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O \ + \ 0,5 \ CO_3^{2-} \ + \ OH^- \ + \ H_2O \tag{38}$$

$$Ca_3Al_2O_6 \cdot CaSO_4 \cdot 12H_2O \ + \ 2 \ Cl^- \ \leftrightarrows \ Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O \ + \ SO_4^{2-} \ + \ 2H_2O \tag{39}$$

$$Ca_3Al_2O_6 \cdot 0,5CaSO_4 \cdot 0,5CaCl_2 \cdot 12H_2O \ \leftrightarrows \ 4Ca^{2+} \ + \ 2AlO_2^- \ + \ Cl^- \ + \ 0,5SO_4^{2-} \ + \ 4OH^- \ + \ 10H_2O \tag{40}$$

Friedel's salt can also form by the reaction of chloride with ettringite, as the reaction represented in equation (41). As can be seen, the chloride reactions with cementitious hydrated products release sulfate ions. This can cause DEF, as shown in section 2.4.1 above [119,121].

$$Ca_3Al_2O_6 \cdot 3CaSO_4 \cdot 32H_2O \ + \ 2Cl^- \ \leftrightarrows Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O \ + \ 2 \ Ca^{2+} \ + \ 3SO_4^{2-} \ + \ 22H_2O \tag{41}$$

Calcium oxychloride is the product of the reaction of chloride and Portlandite, which consumes water, as can be seen in equation (42). This reaction is expansive and causes initially a decrease in the porosity. It is followed by an increase in the number of micro-cracks and the porosity.

$$2 \ Cl^- \ + \ 4 \ Ca(OH)_2 \ + \ 12H_2O \ \leftrightarrows \ 3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O \ + \ 2OH^- \tag{42}$$
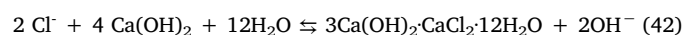
Besides the steel corrosion, a decrease in mechanical strength is observed in samples exposed to chloride attack. Improvements in cure and cement mix formula can help to prevent chloride penetration and minimize its effects on the cement performance [117].

The associated calcium can influence the chloride behavior in the cement matrix. The decrease in the pH of the porewater – as happens when calcium and magnesium are present – increases the chloride adsorption in the C–S–H layers, once the hydroxyl ions are released [116,122].
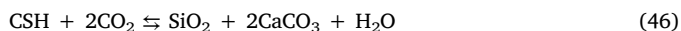
2.4.3. Carbonate attack

The penetration of carbonate ions leads to carbonation of the matrix. The carbonate ions are usually dissolved in the groundwater or come from the atmospheric CO_2. The carbonation rate depends not only on the carbonate concentration but of the pH of the solution, pressure and temperature [123,124].

If this process happens during the cement hydration, it can have a beneficial effect in the material, since the reaction between carbonate and C_3S and C_2S promotes a better hydration and C–S–H formation, as shown in the reactions of equations (43) and (44) [124,125].

$$C_3S + (3 - x)CO_2 + yH_2O \leftrightarrows C_xSH_y + (3 - x)CaCO_3 \qquad (43)$$

$$C_2S + (2 - x)CO_2 + yH_2O \leftrightarrows C_xSH_y + (2 - x)CaCO_3 \qquad (44)$$

When carbonation occurs in hardened cement paste, calcite is formed as the product of reaction with Portlandite. Calcite formation blocks the voids in the cement matrix and prevents the penetration of water. However, at elevated concentrations, the calcium of C–S–H can react with carbonate ions, leading to a C–S–H decalcification and permanent damages to the cement matrix. The reaction of carbonate ions with these Portlandite and C–S–H are represented in equations (45) and (46) [126,127].

$$Ca(OH)_2 + CO_2 \leftrightarrows CaCO_3 + H_2O \qquad (45)$$

$$CSH + 2CO_2 \leftrightarrows SiO_2 + 2CaCO_3 + H_2O \qquad (46)$$

The porosity of carbonated cement samples was reported as lower than the porosity in sound samples by some authors. This leads to a coarsening process in cement pores [128,129]. However, the effects of carbonation and calcite formation on the cement permeability are still controversial. Some authors reported a decrease in cement permeability [130–132], while others reported an increase when the material was exposed to carbonation [129,133,134]. Auroy et al. [124] attributed these differences to the reactions that occurs in the material, which are dependent on the cement type and CO_2 concentration.

The carbonation process has been reported as one process that can also lead to steel bar corrosion. It happens due to the Portlandite depletion caused by carbonation, which decreases the pH value of the porewater and reduces the passivation effect on the steel bar [124,135].
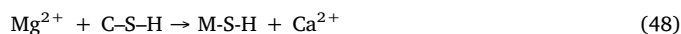
2.4.4. Magnesium attack

The penetration of magnesium into the cement is usually associated with the formation of magnesium hydroxide, known as brucite. The formation of brucite is expansive and can lead to cracking and reduction of cement durability [136,137]. Magnesium reacts with Portlandite to form brucite, as shown in equation (47).

$$Mg^{2+} + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + Ca^{2+} \qquad (47)$$
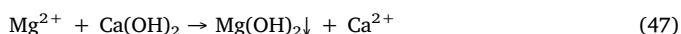
This process leads to a release of calcium ions to the pore water and can increase calcium leaching. Furthermore, brucite is insoluble and causes a decrease in hydroxyl content in the pore water, reducing the pH value and increasing damage [116].

Magnesium ions can also replace calcium in the C–S–H structure, leading to a non-cementitious phase known as M-S-H. The M-S-H formation increases cement porosity and forms cracks in the material, drastically reducing cement durability [138–140]. The replacement of magnesium into C–S–H is shown in equation (48).

$$Mg^{2+} + C\text{–}S\text{–}H \rightarrow M\text{-}S\text{-}H + Ca^{2+} \qquad (48)$$

Both M-S-H and brucite are expansive products that lead to an increase in cement porosity and cracking. When magnesium ions are associated with sulfate and chloride, the synergy between the magnesium attack and sulfate or chloride attack leads to increased damage in cementitious materials [116,122,139].

2.5. The effects of temperature

The exposure to high temperature can affect the durability of cementitious materials. Many research articles address the performance of these materials under or after exposure to fire, when temperatures can rise above one thousand degrees Celsius.

The first effect of exposure to high temperature is the loss of free water that occurs between 30 and 105 °C. Between 110 and 170 °C, gypsum, ettringite and some aluminate phases are decomposed [141–144]. The chemically bound water of C–S–H begins to be lost at 100-120 °C and the loss is progressive as temperature increases. The temperature at which the complete decomposition of C–S–H gel is observed is not a consensus. It has been reported 200-450 °C [145,146], 180-300 °C [144], 600 °C [142] and 900 °C [22]. The C–S–H decomposition cause shrinkage and cracking in the material [143].

Decomposition of Portlandite and formation of CaO is observed at 450-500 °C, causing shrinkage of the material. If it is exposed to water after that, Portlandite can be re-formed leading to cracking [22,142,143,145].

When the temperature reaches 700-900 °C, decarbonation occurs with the decomposition of calcite. Above 1,200 °C, the material is completely decomposed [142,143,146]. The main deleterious effect when cement is exposed to high temperatures during fire is the increase in porosity and permeability of the material, which in some cases are irreversible [142,143,145,147–150].

In a deep repository environment, the temperature will increase above the natural temperature at the repository depth due to the geothermal gradient, as a result of the release of heat from the radioactive decay of the disposed of sealed sources. In a conceptual borehole repository containing the Brazilian inventory of DSRS the temperature of cement grout inside the steel casing was estimated at about 66 °C and in the outer grout (grout backfilling the annular space between the casing and the geological formation) at about 55 °C [151].

At this range of temperatures, one effect on the material is the change in kinetics of hydration during the cure. As shown in section 2.1, high-temperature cure accelerates the hydration process but produces a material with lower final hydration degree, lower mechanical strength and with higher porosity [21,22,35,43].

Some compounds of hydrated cement can be changed chemically and morphologically at temperatures up to 100 °C. Lower mechanical strength, increase in creep capacity, drying shrinkage, pore coarsening, weight loss, and changes in the structure of some compounds were some effects reported under this condition [74,77,152–156].

Although C–S–H water loss begins at temperatures above 100 °C, some studies indicate that structural changes may occur at lower temperatures, down to about 50 °C. These changes, in nanometric scale, lead to C–S–H polymerization, lower superficial area and coarsening of cement pores [152,157].

Ettringite is also affected when the materials are exposed to this temperature, where decomposition and structural changes may occur. Some authors reported the changes in structure starting at 50 °C, while the decomposition may starts at 70-90 °C, leading to C–S–H and AFm phases formation and sulfate release [145,146,154,158–160]. Zhou et al. also indicate the formation of a metastable ettringite at temperatures between 50 and 100 °C [160].

Drying shrinkage is a well-studied effect on cementitious materials.

It results in cracking and can create a preferential pathways for liquid and gas penetration or, in the case of a radioactive waste repository, a preferential pathway for the transport of radionuclides through the cement engineered barrier and out of the disposal facility [161].

The drying shrinkage is a process directly related to temperature and relative humidity. As temperature increases, the relative humidity inside cement pores decreases significantly, leading to the water loss. This loss results in shrinkage by two main processes: the first is the adsorption/desorption process, and the second is by differences in capillary pressure [39,149,157,161–167].

The temperature variation inside the cement had direct influence in thermodynamic properties, like solubility. Many authors reported differences in solubility of cement compounds under a range of temperatures varying from 0 to 100 °C. The AFm and AFt phases have its equilibrium point changed depending on the concentration of ions, and pressure in the material. C–S–H can be formed as many different crystalline compounds. The crystallization of C–S–H can change the Ca/Si ratio, releases calcium and changes other phases of cement. At higher temperatures, a low Ca/Si material is expected [146,157,168–170].

2.6. The effects of pressure

In the borehole environment, the pressure in a given depth increase with the geopressure gradient. The value of the geopressure gradient varies from 25 to 30 MPa per kilometer. In a 400 m deep borehole, the pressure can achieve about 10 MPa [31]. The pressure can increase due to gas generation from some reactions that occur in the repository environment, as radiolysis.

The effects of pressure in deep boreholes have been studied for a long time, due to the use of deep boreholes by oil companies and, more recently, in projects for CO_2 capture and disposal [171–173].

The main effects of pressure on cementitious materials are related to changes in rheological and mechanical properties. Furthermore, high pressure can cause detachment between the borehole steel casing and the cement backfill, forming a preferential pathways for liquid and gas transport [173,174].

Pressure can accelerate the reactions that occur in the cement in its environment, as hydration, acting directly in the reaction kinetics. Specimens of cement paste and mortars exposed to high pressure, showed a higher calcite formation, if in contact with CO_2, and a depletion of Portlandite [172–176].

The rheological properties of cement during the first hours are important because the material has to be pumped into the borehole and the setting time cannot be so quick or slow as to impede a complete and effective borehole cementation. The effects of pressure on properties of cement in early-ages are similar to the temperature effects. The hydration is accelerated during the first hours, due to the acceleration of reaction rates, increasing hydration rate and decreasing the setting time. The final hydration degree is, however, lower than that of un-exposed material [171,177–183].

Empirical results had shown that microcracks could be formed at initial hydration stages, increasing the hydration rates. After some days, however, the density of the material increases with subsequent decrease in total porosity, pore diameter and free water content. However the relative humidity in the capillary pores can increase due to the movement of free water to these small pores under pressure [177–185].

3. Synergy between the environmental factors affecting cement durability

To assess the synergetic effects of all the above-mentioned factors in the long-term durability is a challenging task that needs to be addressed in order to guarantee the repository safety during the required lifetime of the facility.

Three main processes were identified, which can lead to the cement barrier failure: a) the formation of a preferential pathway for the access of water into, or for the transport of radionuclides out of the repository; b) the loss on cohesion and resistance of the cementitious materials; and c) increase in the corrosion rates of steel structures.

An overview of all factors that are involved in these three processes is shown in the conceptual map of Fig. 4. The primary effects, the direct effects of each factor in cement, are detailed in Fig. 5 and secondary effects in Fig. 6.

4. Conclusion

The review performed in this works allows concluding that there are three main causes of failure in the cementitious engineering barriers in a borehole-type repository for radioactive wastes: a) formation of a preferential pathway to water penetration into the repository and transport of disposed of radionuclides out of the repository; b) loss of resistance and cohesion of the cementitious materials; and c) increase in corrosion rate of metallic structures. Regarding each possible failure cause, it can be concluded that:

- A preferential pathway formed between cement and the geologic setting or between cement and the borehole steel casing leads to the escape of gas and the transport of water between the different geological strata crossed by the facility. This increases the deleterious effects in the cement and the corrosion rate of metallic structures;

- The loss of resistance and cohesion occurs because of, for example, cracking that results from increase in cement porosity and changes in cement chemical composition or mineralogy, like decalcification of C–S–H and depletion of Portlandite. The kinetics of these processes may change by increase in temperature and pressure and by the presence of a radiation field. Higher temperatures can lead to loss of cohesion and the formation of non-cementitious phases (as the substitution of C–S–H by M-S-H), which compromises cement cohesion.

- The increase of porosity increases the penetration of water, leading to the leaching of cement compounds, the penetration of aggressive chemicals and reduction of pH in pore water. All these processes boost the corrosion rate of the cement material. Lower pH will reduce the passivation effect of cement on steel and other metals and will affect metallic structures.

- The assessment of the useful life or durability of cementitious materials in the engineered barriers of repositories in the long term depends on the understanding of all the processes that take place and all interactions between materials and processes under the repository environment. To unveil this set of processes is a complex task.

- Based on the conceptual map of interactions between the components of cement and the components of the environment, including materials and forces, the project of modeling the process can be started.

- Forecasting the performance of the structures and assessing the safety of the disposal facility in time scales of millennia depends on our capacity to model those processes to calculate the future states of the cement barrier system.

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