

H₂ generation in cement pastes under gamma irradiation: A state of the art

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Jaroslava Kořátková^{a, b, *}, Jan Zatloukal^a, Pavel Reiterman^a, Karel Kolář^a
and Zbyněk Hlaváč^b

^a Czech University in Prague, Faculty of Civil Engineering, Experimental Centre,
Thákurova 7, 166 29, Prague, Czech Republic

^b Research Centre Řež, Hlavní 130, 250 68, Husinec – Řež, Czech Republic

KEYWORDS

ABSTRACT

Radiolysis

Dihydrogen generation

Cementitious materials

Gamma irradiation

Cementitious materials are exposed to gamma irradiation in many areas such as the concrete structures in nuclear power plants, in medicine or as the cement composites and matrices in radioactive waste repositories. Pore water present in the cement paste undergoes radiolysis due to its interaction with gamma rays leading to dihydrogen production which is in case of a closed systems accumulated in the internal structure of cement paste leading to internal pressure increase. Such phenomenon may influence the material properties or worse if released into operational area it may pose a threat to safety. This article is a review of up to date knowledge, it describes the basic mechanisms controlling radiolysis, presents the main parameters affecting these mechanisms as well as the radiolysis impact on the material properties and ways how to reduce the negative effects of the process. It also addresses gaps in current knowledge and areas which should be in the focus of further research.

Introduction

Considering the significance of nuclear industry, there is a worldwide need to understand the effects of ionizing radiation on cement based materials. Next to neutron radiation, which hazards are limited to concrete structures inside the reactor hall, gamma rays are of significant importance being present and affecting materials in many fields – next to the concrete structures inside the reactor hall of nuclear power plants, these are biological shields in medicine, containers for packages of radioactive waste, immobilization matrix inside these packages etc. [1,2]. Besides the influence of gamma radiation and associated heat on mechanical properties and structural changes of the cement composites, there is a problem of H₂ production due to radiolysis of water in the cement matrix which poses a threat to safety especially in the case of enclosed systems of rad-waste packages.

* Corresponding author: jaroslava.kotatkova@fsv.cvut.cz (J. Kořátková)
<https://doi.org/10.31448/mstj.01.01.2018.18-25>

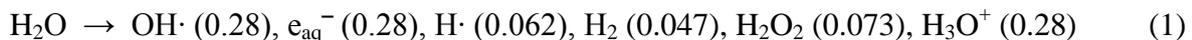
The production of gas may lead to a high pressure build-up affecting the internal structure of cement matrix, causing cracking, lowering the mechanical parameters, changing the gas and liquid transport properties and even affecting the hydration process of cement.

The issue of water radiolysis itself is nowadays well known to researchers however in the cement matrix the process and its intensity is influenced by many factors, e.g. type of radiation source, chemical composition of the cementitious material, dose rate, porosity and so on. The combining of the effects of irradiation, high pH environment and closed system makes it a complex and not easily predictable problem resulting in associated reactions within the cement matrix (such as precipitation or gaseous exchange). The experimental base relating the topic is insufficient to fully understand all the phenomena. Moreover, there is a safety concern relating the risks of H₂ release into the operational area of rad-waste disposal sites [3] which requires the concern of researchers.

Radiolysis governing mechanisms

General reactions

Radiolysis means the decomposition of water molecule due to its interaction with ionizing radiation while generating primary products: i) stable ions and molecules (H₂, H₂O₂, H⁺, OH⁻) and ii) unstable free radicals (e_{aq}⁻, H·, OH·). The primary reaction of radiolysis in normal conditions, i.e. at ambient temperatures and low linear energy transfer rate (LET) can be summarized as [4]:



Where the numbers in parenthesis represent radiation chemical yields (G values; i.e. the quantities produced related to the energy deposited in the mass of water) in units μmol J⁻¹. This is followed by a complex set of secondary reactions of primary products with the species in the pore solution, particularly with OH⁻ producing compounds with a complex chemistry: O⁻, O₂⁻, HO₂, HO₂⁻, etc.

Radiolysis in cement paste environment

In cement, due to the high pH (≈13) certain secondary reactions are modified and become faster since OH· radicals and H₂O₂ are replaced by an oxide radical anions O⁻ and peroxide anion HO₂⁻ respectively, which is beneficial as it results in higher consumption of dangerous H₂. This is however complicated by the presence of impurities, which will be described below [3,5,6,7].

The radiolysis progress in the cement environment is controlled by the precipitation of calcium peroxide octahydrate (CaO₂·8H₂O) [5,6] leading to a significant reduction in O₂ production and indirectly in the decline of H₂ production. Calcium peroxide octahydrate precipitates from the pore solution, which is saturated with Ca(OH)₂, when there is sufficient accumulation of peroxide ions in the solution:



The process described is not systematic and strongly depends on the gamma dose rate being critical between 0.1 and 0.2 Gy/s [5] and temperature with threshold level at 25°C, above which the precipitation stops leading to a non-stationary state resulting in higher O₂ and H₂ production [6].

The generation of dihydrogen is also affected by the pore saturation level (and so on the presence of gas phase) and the initial presence of H₂ [6]. Simulations [6] showed that the higher the saturation level the lower the H₂ production although for fully saturated state no precipitation of CaO₂·8H₂O occurs, which means that the reduction in H₂ production at saturated state is not caused by the presence of CaO₂·8H₂O but by the fact that all of H₂ is present in aqueous phase which is then available for the attack by O^{·-} radicals. On the other hand, very interesting phenomenon occurs, when the initial gas phase for non-saturated pores is created with H₂ as within a few days after a very fast re-equilibration between gases and the pore solution there is an immediate consumption of O₂, while CaO₂·8H₂O has no time to precipitate. The near disappearance of O₂ is followed by a decline in H₂ presence [6].

Origin of water experiencing radiolysis

Effect of waste composition

The chemistry of pore solution present in hydrated cement pastes is influenced by the cement alkaline nature. Therefore, normally the pore solution is rich in calcium and of pH ≈ 13. The generation of H₂ due to radiolysis is also dependent on the water chemistry being higher for water containing Ca(OH)₂ than for pure water [8]. However, the chemistry of pore solution of cemented waste is much more complex and the radiolysis may be affected by every single substance or their interaction. For example nitrates, which are often present in low or intermediate level waste (e.g. evaporator concentrate from cooling systems of PWRs) were recorded to be suppressors of H₂ generation. In the study Bykov et al. [8] the volume of H₂ generation in cement mixed with pure water and NaNO₃ solution was studied (for w/c ratio of 0.25 there was NaNO₃ in the dose of 15 % of cement weight). The dihydrogen yields were recorded to be lower by a factor of almost 30. Conversely, Fe^{II} and Fe^{III} complexes, originating from either parts of solidified rad-waste, cement composition itself, grinding procedure of cement, iron aggregate, either from steel reinforcement, reduce the rate of H₂ and H₂O₂ decomposition. The action of iron is addressed in its own chapter thereafter.

Effect of cement type and its phases

Generally, in the majority of existing research works it has been assumed that the radiolysis of water arises from the pore solution, however radiolysis may occur also in structural water (such as OH⁻ in Ca(OH)₂) or crystallization molecular water (such as H₂O in Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O). There is very little data addressing the issue and thus clear conclusions cannot be made. However, there has been a research in CEA, France conducted by L. Acher et al. [9] studying the role of individual phases in the radiolytic yields of H₂ production – G (H₂). Pure hydrates were exposed to gamma irradiation at a dose rate of 600 Gy/h up to 1MGy. It was observed that next to the nature of the hydration product, the radiolytic yields are affected also by the storage humidity which is demonstrated in Figures 1 and 2. The results indicate that the majority of H₂ production is caused by radiolysis of water bonded in C-S-H compared to other phases typical for Portland cement. Crystalline water (such as H₂O in CaSO₄·2H₂O) seems to be more easily decomposed by gamma radiation than structural water (OH⁻ in hydration products). L. Acher also stated in the follow-up works [10] that radiolytic yields also depend on the water/cement ratio as there was about 45 % higher values for Portland cement paste with w/c = 0.6 compared to w/c = 0.2, which suggests the non-negligible role of structural and crystalline water in the radiolytic process. However, the action of structural and crystalline water probably depends on the irradiation dose rate and accumulated dose. An experiment held in Japan [2] showed that the G-values of hydrogen

release stayed in case of pre-dried specimens very low throughout the whole irradiation period of 61 days even for very high dose rate of 7.05 kGy/h, which means that crystalline or structural water were not attacked by radiolysis.

Coming back to Acher's research [10], comparison of the behavior of different types of cement was made, namely of Portland cement, calcium-aluminate cement (Cement Fondu) and phospho-magnesium cement. The recorded values of radiolytic yields were considerably higher for Portland cement compared to the other types of cement which was governed by the nature of hydrates, as C-S-H and ettringite, the products of Portland cement hydration, seem to experience radiolysis in much higher extend than AH_3 and C_3AH_6 , the products of calcium-aluminate cement hydration, or K-struvite, the hydration product of phospho-magnesium cement (Figure 3). However, it should be noted that this also depend on the w/c ratio, as in case of Cement Fondu, there is a significant increase in radiolytic yields when the water content exceeds a critical value [10].

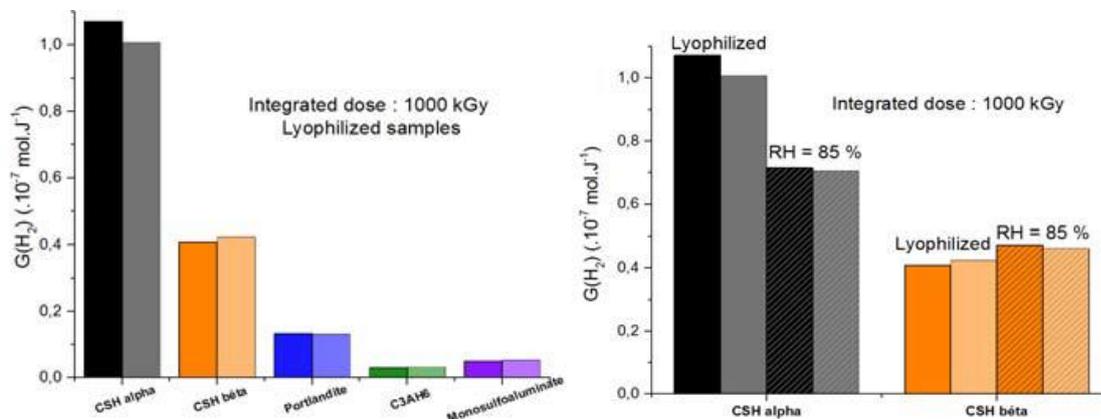


Fig. 1 and 2: Radiolytic yields $G(H_2)$ in $\text{mol} \cdot \text{J}^{-1}$ obtained for different cement phases and storage conditions (taken from [9])

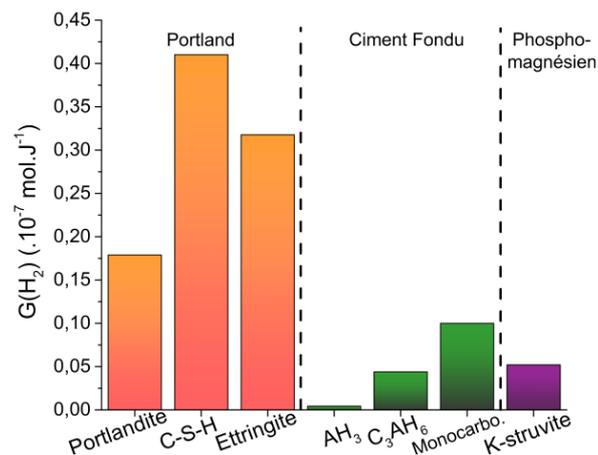


Fig. 3 Comparison of radiolytic yields $G(H_2)$ in $\text{mol} \cdot \text{J}^{-1}$ obtained for Portland cement, calcium-aluminate cement (Ciment Fondu) and Phospho-magnésien (taken from [10])

Blast furnace slag cements (CEM III/C) contain sulfides which modify the pore solution chemistry affecting the chain of reactions. A study was made in France to clarify the influence of sulfides on radiolysis process on BFS-cement pastes exposed to gamma irradiation for 6 months at a dose rate 356 Gy/h in a closed system without oxygen [11]. An increase of H_2

production (in comparison to Portland cement pastes) was observed in the first two months of irradiation. In this period of time sulfides converted into polysulfide anions leading to an increase in pH followed by a reaction at a very high speed:



However, later on, the sulfides concentration becomes insufficient and the sudden reducing environment initiates efficient recycling of H_2 which was supported by high level of pore saturation. Thus in long term, the radiolysis effects are reduced.

Hydrogen transport through cement paste

The transport of hydrogen is controlled either by free (or Knudsen) diffusion, molecular diffusion or by diffusion through water. The transport mode is dependent on the porous system of the cement matrix especially on the pore size and on the water saturation level [12]. These are influenced by the mix design and storing conditions, mainly relative humidity. According to [12] the saturation level does not restrain the diffusion of hydrogen until it reaches level of 0.6, above which the diffusion coefficient progressively decreases. It was also concluded that the diffusion of hydrogen is controlled by the saturation of smaller pores which are randomly connected to bigger ones. The H_2 generation within the closed system of cement matrix induces a pressure rise in its internal structure, while the change of the internal conditions may influence the gas transport properties [2].

Effect of radiolysis on cement paste properties

The strength of cement paste can be indirectly influenced by radiolysis. In case of favorable conditions (as described above) calcium peroxide octahydrate precipitates in the pore solution and can further decompose leading to carbonation of cement paste through a set of reactions:



Carbonation leads to decrease in porosity by filling up the pores by CaCO_3 which usually results in the increase of strength, both compressive and flexural as in [2]. Unlike in the case of carbonation of cement on air, the process occurs in the whole volume of the composite and it is not limited to its surface [13]. Nevertheless, different effects on the final compressive and flexural strength of concrete were obtained from different research studies. Meanwhile Vodák et al. [14] reported a decrease in both parameters with increasing irradiation dose up to 600 kGy, Maruyama et al. [2] observed increasing of both parameters when irradiated to doses up to 200 MGy. Maruyama et al. [2] suggested that the increase of strength was due to the formation of aragonite and vaterite as the product of carbonation instead of calcite, while the C-S-H layered structure is not affected unlike in the case of the well-known carbonation on air, which destroys the C-S-H structure. However, the true processes affecting the cement paste strength has not yet been understood and obtained data varies from one research work to another [2,14,15].

If the cement paste is exposed to gamma irradiation in the early stage of its maturation, it may affect the hydration process as the disappearance of H_2 and O_2 due to radiolysis could lead to

lower hydration degree and eventually lowering the strength and affecting other properties such as porosity etc. [15].

The role of concrete reinforcement

As mentioned above, during radiolysis many secondary reactions occur, which may lead to rise of corrosive substances such as O₂ and H₂O₂ and thus the radiolytic process may lead to depassivation of concrete reinforcement. However, there is also not much data relating the problem. The study of V. Dewynter et al. [16] showed very low corrosion rate of embedded rebars in cements type I and V due to radiolysis of samples under irradiation with dose rate around 15 Gy/h for the duration of 12 months which represented a cumulated dose up to 3.10⁵ Gy. The corrosion rate in CEM I was slightly higher (0.25 μm/year) than in case of CEM V (with values between 0.1 μm/year and 0.2 μm/year).

The presence of iron in the pore solution, which is locally enhanced due to the dissolution of rust products on the rebars' surface, also modifies the radiolysis chemistry as iron disturbs the chain of reactions. Radicals O^{·-} and e⁻_{aq}, which at normal conditions react with H₂ and HO₂⁻ respectively, accelerate the reaction chain resulting at H₂ recycling:



However, Fe^{II} and Fe^{III} species are more likely to attract and react with these radicals:



This unfortunately results in decreasing the recycling effect and thus in higher dihydrogen accumulation [17].

Modelling of radiolysis

Bouniol et al. [5] reviewed the basic mechanisms of dihydrogen production process in cement matrices and came up with a comprehensive model describing radiolysis at specified conditions, i.e. in a closed system, at temperature 25°C and with a pore solution representative of a Portland cement paste. The code CHEMSIMUL [18] was used to simulate different scenarios varying in dose rate, liquid saturation level in the cement porous system or in the initial amount of H₂ present in the gas phase of the closed system [5]. Later on, this model was upgraded with a module, preliminarily addressing the influence of iron species, however it requires readjustments and complements for making good predictions [19]. In connection with this, the collaboration of CEA and EDF was made, which aimed at understanding the radiolysis phenomenon and gave rise to a model called DO-RE-MI (Description Opérationnelle de la Radiolyse de l'Eau dans les Matériaux Irradiés). The model was applied to a theoretical package for a parametric study to characterize main parameters affecting H₂ generation [20]. The drawn conclusions were: a) the higher the porosity of cement matrix, the higher the H₂ generation probably due to the higher content of water present in the pores; b) the process depends on water saturation level being critical for 0.64; c) higher dose rate increases the radiolysis effects; d) the presence of iron strongly enhances the dihydrogen formation for water saturation levels above 0.64 (up to 100%), however for low saturation

levels, the iron effect is negligible as in both cases (with or without iron) no recycling of H₂ occurs.

Summary

Radiolysis occurring in a closed system of pores inside cement paste due to gamma irradiation of concrete or cement immobilization matrices for radioactive wastes may impose safety risks relating the H₂ generation and its release into the operational area of rad-waste disposal sites or it may lead to change of properties of the materials being affected. Proper understanding of its effects is therefore of vital importance, however the up-to-date data addressing the issue are insufficient for precise prediction of all possible scenarios. The paper presents a state of the art summarizing the current knowledge and denotes gaps and areas which requires further investigation.

Acknowledgement

This work was financially supported partially by the Czech Science Foundation, under project GA17-11635S, the Czech Technical University in Prague - project No. SGS16/199/OHK1/3T/11 and by Ministry of Education, Youth and Sport Czech Republic - LQ1603 Research for SUSEN under projects CZ.1.05/2.1.00/03.0108 and CZ.02.1.01/0.0/0.0/15_008/0000293.

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