Cemented waste deterioration by delayed ettringite formation: chemistry and effect on structural and mechanical properties

1. BACKGROUND CONTEXT

For decades, the nuclear industry has used cement-based materials to immobilise low- and intermediate-level short-lived and long-lived radioactive waste (precipitation sludge, concentrates, resins, etc.) originating from the operation of nuclear power plants and from the chemical reprocessing of spent fuel [1]. Such conditioning processes for the radioactive waste would stabilize the waste form which needs to comply with acceptance criteria for the final disposal. However, this is not necessarily the case, as evidenced, for instance, by the gel formation attributed to alkali-silica-reaction (ASR) in the concrete operational waste of the nuclear power plant of Doel [2].

During waste immobilization using cement binders, one could encounter a number of deleterious processes that threatens the integrity of the final matrix. Delayed ettringite formation (DEF), which is essentially a heat-induced internal sulphate attack, is one such deleterious process, which may lead to volumetric expansion and hence cracking. This process is of utmost importance to the Belgian national programme for nuclear waste disposal because of the sheer volume of waste that needs to be safely immobilized.

In fact, it turns out that DEF is one of the most controversial topics because there is still no consensus on the mechanism of expansion due to DEF ([3] cited in [4]).Though, there is a clear consensus on the chemical reaction mechanism itself and the influence of various factors such as temperature, higher alkali content, initial sulphates in the mix, etc. on the expansion. It is worth mentioning that currently there are two contradictory schools of thoughts: (i) *massive* ettringite generation yielding high re-crystallisation pressures that lead to expansion/cracking [5], and (ii) *homogeneous expansion of cement paste* due to nanoscale ettringite formation in C-S-H gel, which leads to expansion/cracking [6].

The existing knowledge base is purely driven by the civil engineering community for construction applications, where, in order to minimize DEF, various precautionary measures are proposed concerning the amount of C_3A, SO_3, gypsum, alkalis and temperature (< 60 ºC), with further recommendations on the use of supplementary cementitious materials to reduce the heat of hydration and on curing techniques. However, even with the above precautions, some researchers have noted that some cement/mortar/concrete types may undergo DEF related expansion. This leads to a conclusion that there are several confounding factors that influence the link between expansion and DEF (see Figure 1).

The issue becomes even more complex when applied to nuclear waste. In Belgium, various radioactive waste forms containing sulfates, such as ashes from incineration facilities, sludges and liquid effluents, ion exchange resins or concrete debris can be encountered. Prior to their disposal, most of these radioactive wastes will have to be properly conditioned using a cement-based material. Due to diversity of the possible waste forms and their characteristics (e.g. liquid/powders/solid, activity levels, and chemical forms of the sulphates), various parameters would lead to DEF phenomena specific to the cementation of such wastes. Moreover, because large volumes of waste are to be immobilized, there is a possibility that the heat of hydration exceeds the threshold value (60 ºC). Therefore, it is clear that a new research study is warranted to develop phenomenological understanding of DEF of the immobilization matrix for such radioactive waste forms. This is the objective of this PhD.

2. RESEARCH QUESTIONS

There is a considerable number of open questions concerning DEF of the immobilization matrix system with high sulphates. Salient ones are listed below, which are predominantly taken from the synthesis of data by [7] for a/the traditional cement-pore water system and seen as relevant for this PhD programme. However, during the initial phase of the PhD project, these questions have to be re-visited to narrow down the scope of work.

2.1 PHENOMENOLOGY AND EFFECT ON MECHANICAL PROPERTIES

a. *Microstructural and mineralogical effects*: The microstructural changes induced by DEF in the immobilization matrix system with high sulphates are not yet completely known and understood, and hence this forms the most important research question to address within this PhD programme. An interesting observation by [8] states that ettringite formation is stabilized (thermodynamic equilibrium) in the presence of very high sulphate concentrations. Which is this stability point and is the matrix already damaged before reaching this point? Recall that there are two schools of thoughts. It is interesting to investigate to which school of thought this research leads to.

b. *Link between DEF and expansion*: A challenging task is to develop a quantitative understanding of the link between the amount of ettringite formed and expansion, which has remained elusive so far [9, 10, 11].

2.2 INFLUENCING PARAMETERS

a. *Alkali content, sulphate content and pH*: This also relates to *Microstructural effects*. How does the concentration of Na, K, Mg and sulphates, and pH affect DEF? It is well-known that a higher alkali content leads to larger expansion and hence cracking [12], but it may inhibit the ettringite formation when present after reaching peak hydration heat generation [13]. Note that the presence of other ions in the pore water may also affect the extent of DEF [10].

b. *Temperature threshold*: Research has so far suggested that to avoid DEF, the safe operating range for temperature is below 60 ºC (sometimes 70 ºC is reported). How far is this true given the initial high sulphate system? Currently, ONDRAF/NIRAS follows the 60 ºC criterion stipulated in the waste acceptance criteria. Is this a conservative approach? If the temperature is well above the threshold value, then what will be the effect of a given (sufficiently long) duration of a high temperature regime?

c. *Temperature threshold in the presence of supplementary cementitious materials (SCM)*: Research suggests that adding BFS, SF or FA can almost stop DEF because of the very low heat of hydration ([14], [15] and [16] cited in [7]) and lower initial alkali content. Is it possible to quantify the acceptable range of proportions of these SCMs?

d. *Aggregate type*: Research shows that limestone aggregates can significantly reduce DEF compared to quartz aggregates ([17] and [18] cited in [7]). Is this still true for the cement-waste matrix system? What is the effect of aggregate size, for instance, limestone fillers, on the risk of DEF and thaumasite formation?

e. *Effect of restraint*: Research shows that under external restraint the DEF effect on expansion is limited and anisotropic in nature. However, under stress free conditions there will be an isotropic expansion [19]. Quantification of this behaviour for the cement-waste matrix is thus warranted.

2.3 PROPERTIES

a. *Mechanical properties*: It is well-acknowledged that a single measure for DEF effects such as expansion (see 2.1b above) is not sufficient to interpret the behaviour of a material [10]. Therefore, in addition, mechanical properties such as modulus of elasticity, compressive strength are also necessary. The following questions therefore naturally arise:

   How does the modulus of elasticity and compressive strength change as a function of DEF? It is commonly cited that the modulus of elasticity decreases with increase in ettringite content, but later it regains its original value when ettringite growth has ceased [20]. *For* instance, in the work of [21], it is stated that if swelling exceeds 0.1%, one could expect a drop in the dynamic modulus by 60% and by 70% in the compressive strength. Therefore, a quantitative picture of these mechanical properties is necessary from the point of view of mechanical stability of the high sulphate matrix.

3. OBJECTIVES

The principal objective is to develop mechanistic and phenomenological understanding of the chemistry of delayed ettringite formation (DEF) and its effect on mineralogical changes, microstructural changes and mechanical properties of the cement-waste matrix system with high sulphates, to address some of the research questions identified in Section 2 above.

4. RESEARCH METHODOLOGY

The following steps are envisaged, however, to be revisited during the start of this PhD programme.

a. *Literature survey*: to explore the state of the art in the degradation mechanism of DEF and experimental techniques to measure the effects of DEF.

b. *Choice of cement system and waste composition*: For the cement system, this involves cement type, aggregate type, and addition of SCMs. For the waste composition, this may involve variations in the sulphate content and alkalis. One may be tempted to follow the route of full factorial design of experiments. However, as clearly suggested in [13], it is best to carry out local sensitivity analysis (in other words limit simultaneous variations of design parameters) to gain a better understanding of the phenomenology of DEF. The proposal is to consider a low C_3A cement (CEM I) and consider various proportions of SCMs, but in an incremental manner.

c. *Thermodynamic calculations*: A geochemical model (with appropriate cement thermodynamic database) will be used to understand the potential for DEF for various ionic compositions. This is to help in the initial choice of formulation.

d. *Design of test cells*: Adaptation of the existing SCK•CEN test cells (used for the study of bituminised waste) to measure the expansion (under constant stress conditions) or pressure (under (nearly-)constant volume conditions) for a degrading cemented waste form. Adaptation not only includes special consideration for the cement-waste matrix but also temperature control.

e. *Oedometer and load cell tests*: Conduction of tests in the newly developed test cells to measure the expansion or the pressure at regular intervals.

f. *Characterization tests*: Conduction of tests to study mineralogical, microstructural and mechanical properties of the waste. Envisaged characterisation techniques are XRD, SEM-EDX, thin layer petrography, SIMS, MAS-NMR, N2 adsorption, MIP, etc. Other analysis techniques may become necessary as the project proceeds (e.g. non-destructive testing and visualization of crack development), and some will have to be subcontracted to or to be performed in collaboration with external partners (CEA, PSI, etc.).

5. CHALLENGES

DEF is a slow process taking weeks, months or even years to manifest, depending on the formulation of the cement-waste matrix. A downside to accelerated DEF tests is that it will not be representative of realistic conditions because of different reaction paths [10, 13]. This is to be avoided, if possible. Some suggestions are therefore highlighted below:

a. The water uptake cells in combination with oedometers and very sensitive logging of *swelling* in the SCK•CEN laboratory with well-controlled (quite stable) temperature environment offers the possibility to study even a small change in volumetric deformation behaviour of the test samples. Furthermore, periodic characterization of various test samples provides transient response of the partially degraded cement-waste matrix. In this way, it is hoped and expected that even though the actual tests may continue for longer than the allowed PhD duration, there will be sufficient data to make meaningful conclusions. Furthermore, based on existing data, the formulation of the cement-waste mix will be designed in such a way that the duration of DEF experiments are kept to a reasonable length of time.

b. In order to simulate realistic conditions, i.e. in terms of heat evolution in the core of a waste drum and natural dissipation of heat with time, a combination of numerical and experimental approach can be adopted. Experimentally, the test samples can be cast and allowed to hydrate under adiabatic conditions until the temperature output reaches an asymptotic value. Following this, the samples are shifted to the test cells. Here there are two possibilities: (i) carry out the experiment under semi-adiabatic conditions as dictated by laboratory environment, or (ii) numerically simulate the heat dissipation from the core of the waste drum and use this as an input to artificially control the heat dissipation in the test cells.

c. The size of test samples also affects the length of experiments [10]. Therefore, the approach is to consider smaller sized samples, keeping in mind the representative volume element as well as test cell design constraints, if any.

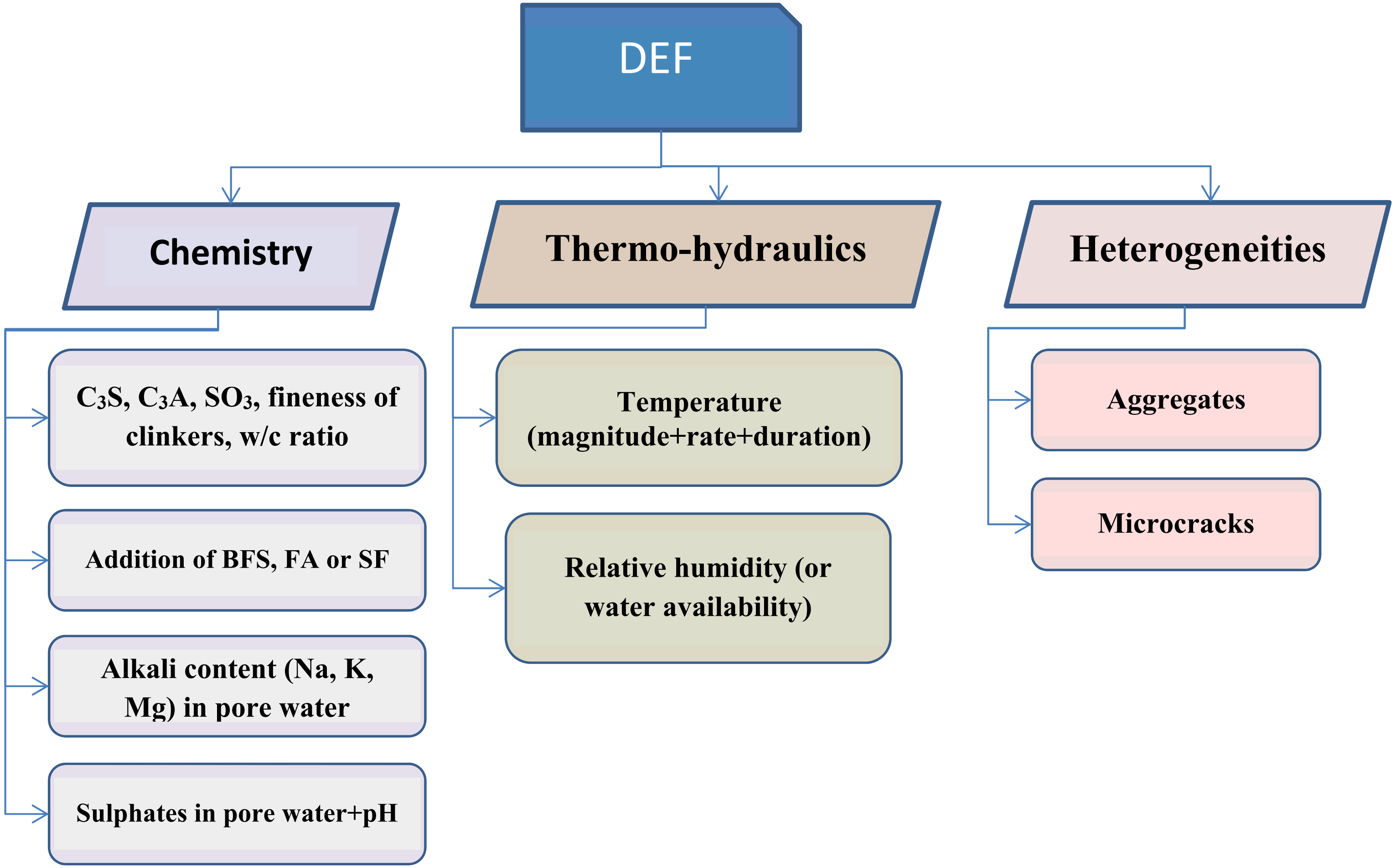

Figure 1: Some of the interacting factors affecting DEF (not exhaustive).

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