

A PHENOMENOLOGICAL MODEL FOR HYDRATION HEAT EVOLUTION OF A CEMENTED WASTE FORM

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Abstract

This paper presents an extension of an existing phenomenological model for predicting the evolution of hydration heat of a cemented waste form. The cemented waste form is essentially a mixture of blended cement and homogeneous low- and intermediate-level liquid (simulant) radioactive waste (sludge). The motivation stems from the fact that the existing empirical or phenomenological models are not designed to handle the interaction of a blended cement system with the waste sludge. The main objective of the proposed model is to minimize the number of isothermal or semi-adiabatic experiments (and thus the cost) required to design a promising recipe for conditioning the waste form. The paper demonstrates the capability of the model to successfully predict the evolution of hydration heat for various cemented waste form recipes.

Keywords: Hydration heat, Cement, Sludge, Supplementary cementitious materials, Radioactive

1. INTRODUCTION

Blended cements are promising candidates for conditioning of homogeneous low and intermediate-level liquid radioactive waste (very often this is a sludge). The conditioning is typically carried out at industrial scale in disposal containers with a capacity of several hundreds of litres. This means that at the core of such containers, temperature can rise to high levels depending on the formulation of blended cement as well as any additional exothermal heat generated due to cement-waste interaction, and this despite the heat reduction benefit of blended cements. It is therefore important to ensure that the peak temperature in such containers does not rise above a certain threshold (~ 60 °C) to avoid the risk on formation of delayed ettringite and thermal cracking.

The evolution of the hydration heat can be studied via the use of isothermal/semi-adiabatic/adiabatic calorimeters. In this work, a combination of isothermal calorimetric measurements on various blended cements and sludge, and an adapted stoichiometry-based phenomenological hydration heat model [1] is applied to predict the evolution of the hydration heat of a cemented waste form using blended cementitious materials composed of blast furnace

slag, silica fume and ordinary Portland cement. The model has a number of parameters, which are calibrated, in a step-wise manner as in [1], against a specific set of isothermal calorimetric experiments. With the calibrated parameters fixed, the model's performance is examined against several other isothermal experiments.

2. PHENOMENOLOGICAL MODEL FOR HYDRATION HEAT

In a blended cement binder system, the total heat evolution ($Q(t)$) is attributed to the heat contributions from different exothermic reactions of binders such as ordinary Portland cement (OPC), blast furnace slag (BFS), silica fume (SF), etc. during hydration. Therefore, the enthalpy of reaction of binders $Q_{\infty,i}$ (assumed independent of temperature), weight fraction of binders in the total mixture (f_i), and degree of hydration of each binder (α_i) are needed to compute the total heat evolution. This can be mathematically expressed as:

$$Q(t) = \sum_{i=1}^n \dot{\alpha}_i f_i Q_{\infty,i} \quad (1)$$

where $\dot{\alpha}_i$ is the rate of hydration degree of the cemented waste form, which needs to be estimated. In this study, the phenomenological model proposed by Kolani *et al.* [1] (and references therein) is used (Eq. 2). However, an extension is proposed to include the effect of sludge (sludge loading) by introducing an additional variable w_i .

$$\dot{\alpha}_i = A_i g_i \pi_i h_i S_i w_i \quad (2)$$

where $\dot{\alpha}_i$ is the rate of hydration degree, A_i is a constant that needs to be calibrated, g_i is the chemical activation term, which is a function of volumetric concentration of clinker and of water in the cement paste, π_i is a function that accounts for water accessibility of anhydrous clinkers, which is a function of volumetric concentration of hydration phases, anhydrous phase, porosity and free water volumetric concentration in the cement paste, h_i is a function that accounts for temperature effects via Arrhenius equation, and S_i is the delay function to account for the addition of supplementary cementitious materials. Note that in addition to A_i , there are three more calibration parameters associated with the variables of Eq. 2. The strategy for calibrating these parameters is the same as that adopted in [2], *i.e.* the parameters for OPC are first calibrated with the isothermal experiments on pure OPC. These are kept constant and the parameters for BFS are calibrated with the isothermal experiments on OPC-BFS blended system, and so on.

3. CALIBRATION AND VALIDATION

A number of isothermal experiments on pure and blended mixtures, including mixtures with waste sludge have recently become available [3]. Table 1 presents a list of isothermal experiments used for calibration of parameters and validation.

Fig. 1 shows the effects of w/c ratio and BFS replacement level on the cumulative heat release after 7 days of hydration at 20 °C. The heat is normalized by the mass of cement and BFS in each sample. It can be seen that the predicted results are in good agreement with the measured data. Both modelling and experimental results show a small difference in cumulative heat release of samples with w/c ratios of 0.7 and 0.9 (Fig. 1, left). For pure OPC, the two curves overlap during an initial period of around 20 hours. After this period, modelling results show that the sample with lower w/c ratio of 0.7 exhibits a slightly lower heat release, but

experimental data still show the overlapping. It is commonly shown in literature that for low w/c ratio samples (less than 0.45), despite similar cumulative heat release in the initial hydration period, samples with lower w/c ratio produce lower cumulative heat [4, 5]. This phenomenon is typically explained by the reduction in the amount of available water and space for hydration in a system with low w/c ratio. However, if the w/c ratio continues to increase, the effect of w/c ratio on the hydration rate becomes negligible, as seen for the samples with high w/c ratios of 0.7 and 0.9 in this study.

It is not surprising that the addition of BFS reduces the heat release, and the higher the BFS replacement level, the lower the cumulative heat release, as seen Fig. 1 (right). This is consistent with a lower heat release due to the presence of BFS, which is confirmed in the majority of published research [1, 6]. Note that if normalized to the cement content, the heat release is higher with the increase of BFS replacement levels and much higher than the one of OPC sample with the same w/b ratio. The heat increase (normalized to cement content) is explained by the acceleration of the clinker hydration in the presence of BFS and the exothermic reaction of BFS itself. Compared to OPC, besides the first (rapid reaction) and the second hydration peak associated to OPC (mainly alite) hydration, a third hydration peak can be recorded for the mixes containing BFS, as shown in Fig. 2. This peak corresponds to the slag reaction in an alkaline environment created by the OPC hydration (e.g. C₂S, C₃S), which liberates a significant amount of calcium hydroxide. The second peak also appears quicker for the BFS mix.

Table 1: Mix formulation

Material	OPC Wt%	BFS (SL) Wt%	Silica Fume (SF) Wt%	Sludge (Slu) V%
Used for calibration				
OPC1(w/c = 0.9)	100	0	0	0
SL 1 (OPC-BFS)	70	30	0	0
SL 1, SF1 (OPC-BFS-SF)	60	30	10	0
SL 1, SF 1, Slu 1 (OPC-BFS-SF-Sludge)	60	30	10	50
Used for validation				
OPC2 (w/c = 0.7)	100	0	0	0
SL 2 (OPC-BFS)	50	50	0	0
SL 2, SF 2 (OPC-BFS-SF)	30	50	20	0
SL 2, SF 2, Slu 2 (OPC-BFS-SF-Sludge)	30	50	20	45

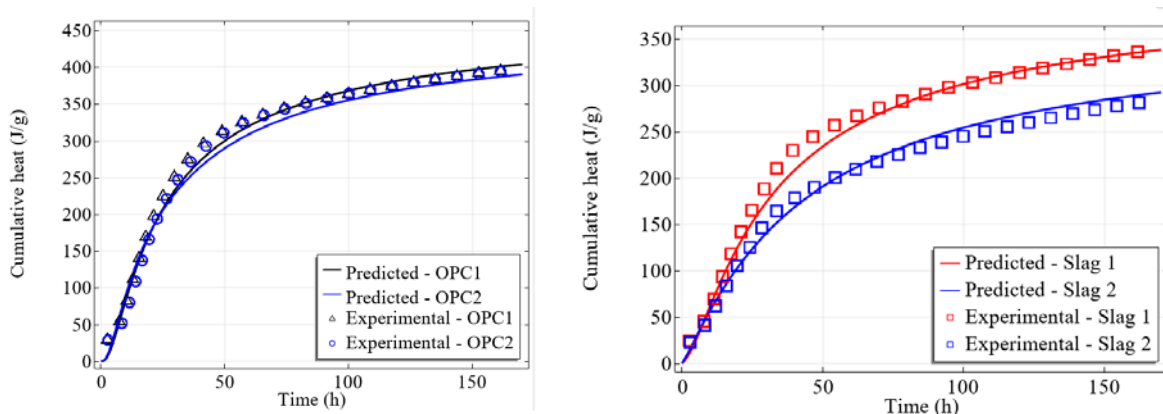


Figure 1: Comparison of experimental results vs. prediction for pure OPC formulations (left) and OPC-BFS mix (right)

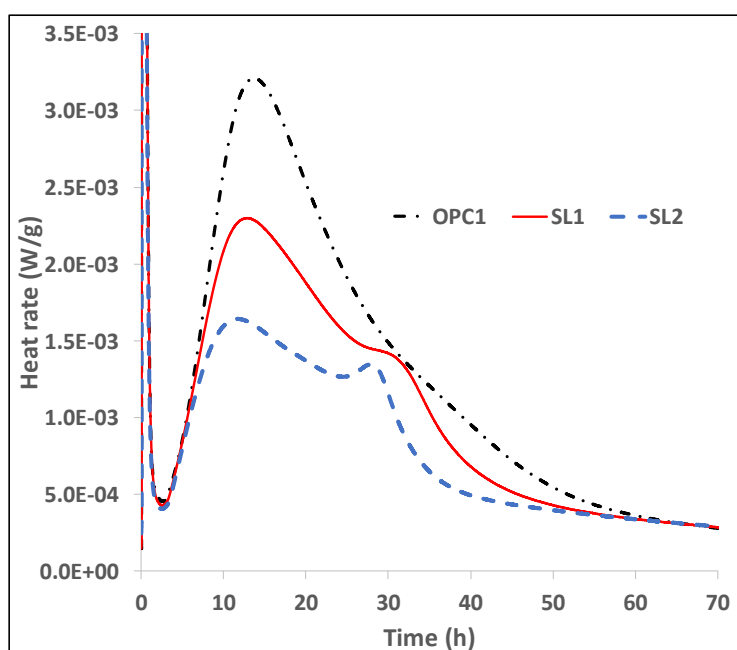


Figure 2: Comparison of experimental heat rate of OPC vs. BFS mix

Fig. 3 illustrates the predictive capacity of the model when the system becomes more complicated, e.g. adding 2 supplementary cementitious materials (BFS + SF) and sludge. The model is again able to capture the cumulative heat release for a blended system with or without sludge quite well, except for the case SL2_SF2_SLu2, which is slightly underestimated after 80 hours of hydration. It is also observed that the addition of sludge results in an increase in cumulative hydration heat, due to possible exothermal reactions occurring between the sludge and cementitious matrix, which is well captured by the model.

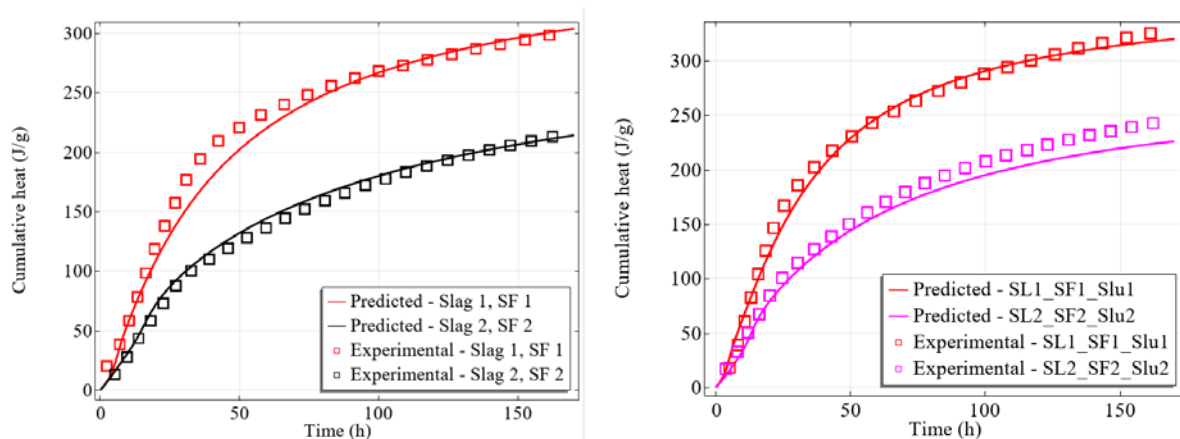


Figure 3: Comparison of experimental results vs. predicted solution for OPC-BFS-SF (left) and OPC-BFS-SF-Slu mix (right)

8. CONCLUSIONS

Using a combination of isothermal calorimetric measurements on various blended cements and sludge, and an adapted stoichiometry-based phenomenological hydration heat model, it is possible to predict the evolution of the hydration heat of a cemented waste form. The proposed extension to the stoichiometry-based phenomenological hydration model (multiplicative law) essentially accounts for the additional effect of simulant radioactive sludge to the hydration heat. It is interesting to note that the new model is able to reasonably capture the evolution of hydration heat of various cemented waste form recipes.

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