

Evolution of the Mass Balance of Water in the Hardening Process of Cement Compositions

D. Stackelberg and B. Wilge

Concretec Ltd., Yavne, Israel

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Introduction

Hardening and strengthening of cementitious materials is the result of simultaneous growth and interaction (in the thermodynamic sense) of chemical and structural transformations [1]. The source material, a visco-plastic mixture, gradually transforms into artificial stone with dominating elastic properties.

A characteristic feature of the hardening of cement systems is the interaction between their liquid and solid phases. The liquid phase – the pore-filling solution, is a structural component, which *binds together* solid-phase elements of different dimensions and configurations. The structured liquid phase is a dispersed matrix-like medium that has a direct contribution to the strength balance of the material.

In addition, the liquid phase possesses a highly important property: it is always in a state of thermodynamic equilibrium with the solid phase onto which it is adsorbed (or by which it is absorbed). For this reason, structured physical water (mixing water minus chemically-bound water) is the most informative component of hardening cement-concrete compositions: any change in its condition adequately reflects the dependencies of structure development, and therefore – of strengthening during all stages of hardening.

It must be noted that physical water is not of homogeneous structure and properties. Thus, according to the “gel-space” concept of T.C. Powers [2], the overall mass of water in cement paste, m , is composed of chemically-bound m_{ch} , evaporable m_{evp} and non-evaporable water. In turn, evaporable water is composed of capillary water m_L and gel water m_g ; in other words:

$$m = m_{ch} + m_{evp} + m_{non-evp} = m_{ch} + m_L + m_g + m_{non-evp} \quad (1)$$

The hardening process of cement compositions is characterized by continuous quantitative and qualitative changes in the mass balance of structured water (1). Variations in the components of the balance of the liquid phase, which is in equilibrium with solid surfaces, occur as the solid skeleton of the hardening material forms. In practice, these variations are realized as transformations of one type of water into another, for example, $m_L \rightarrow m_{ch}$.

The aforesaid suggests that the process of structural formation and hardening of cementitious materials can be studied experimentally and described analytically by studying the dependencies

of formation and transformation of the moisture composition. These changes occur as a result of redistribution of the structured water in the volume of the forming capillary-porous structure.

Results and discussion

The analysis of mass balance evolution during the hardening process of cement materials was carried out based on the experimental results of work [3]. W.P. Halperin *et al.* used an NMR method to study the hardening of white cement paste with water to cement ratio $W/C = 0.43$ over 1500 h. Based on the measurement of spin-spin relaxation of hydrogen atoms, the authors determined the variations in the quantity of evaporable water, the specific surface of hydration products and the mean radius of pores in the hardening process.

Based on these results, and using the formulas of T.C. Powers [2], we calculated the variations in moisture mass balance components m_{ch} , m_L , m_g and m_{non-ep} (1) in the process of cement paste hardening. The results of the calculations are presented as a kinetic diagram in Fig. 1.

The diagram shows that the chemical bonding of water ($m_{ch} \rightarrow \max$), the formation of thin adsorption films of liquid on hard surfaces ($m_{non-ep} \rightarrow \max$) and the formation of cement gel ($m_g \rightarrow \max$) occur owing to a decrease in the mass of capillary water ($m_L \rightarrow \min$) as a combination of the following transformations:

- $m_L \rightarrow m_{ch}$ – transformation of bulk capillary water into a solid-phase state during processes of chemical bonding,
- $m_L \rightarrow m_{non-ep}$ – transformation of bulk capillary water into a strongly-bound state of thin adsorbed layers,
- $m_L \rightarrow m_g$ – transformation of bulk capillary water into a strongly-bound state of gel water.

By differentiating equation (1) in time, we can determine the rate of transformation of each component in the balance. Comparison of the rates allows us to evaluate the correspondence between the progress and the history of the processes. For example, we can evaluate the correspondence between the gel formation process and the nature and intensity of chemical bonding. In light of this, we have the possibility of exerting directed regulation of the transitions between the balance components using chemical additions and other methods.

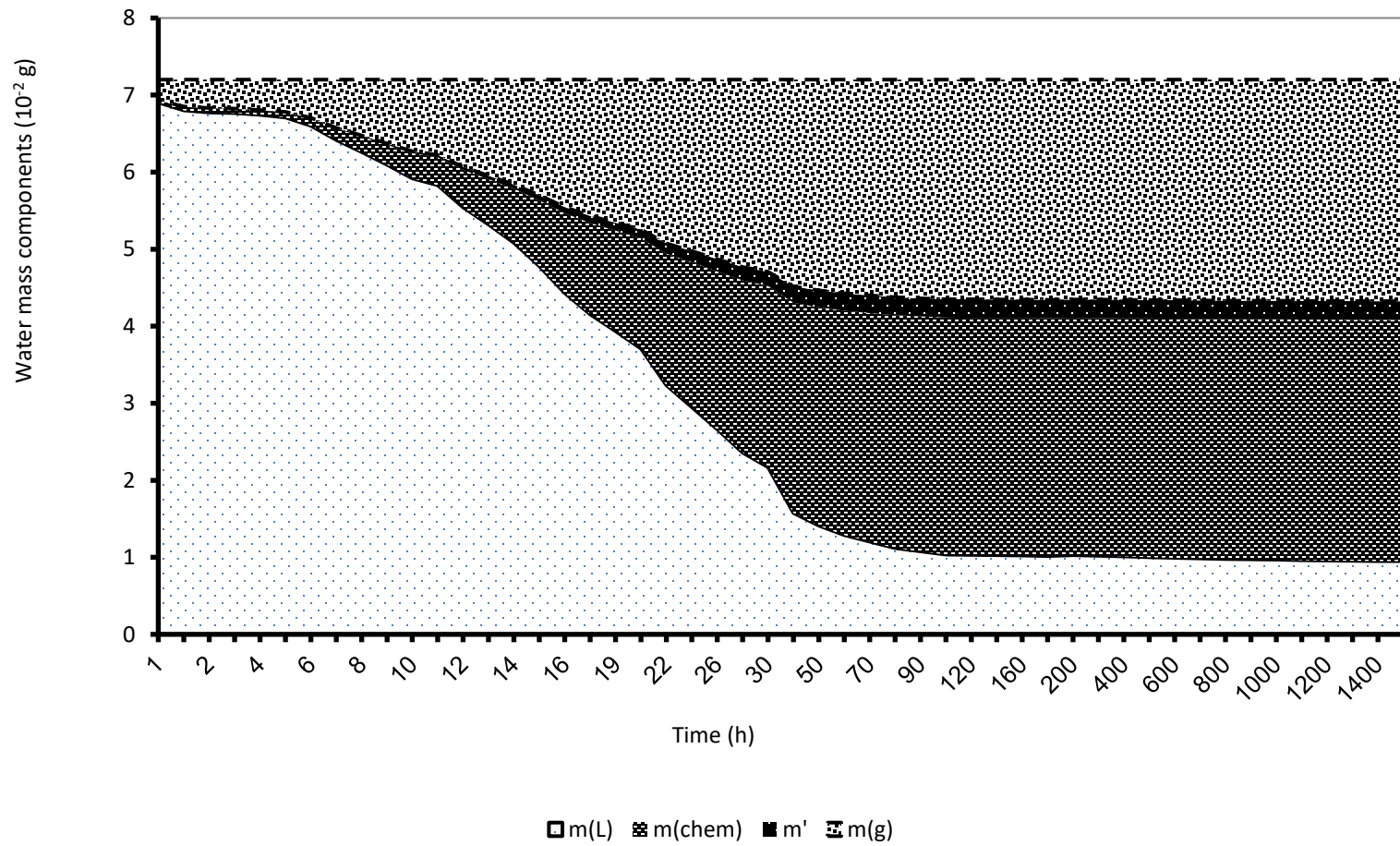


Figure 1. Kinetic diagram of water mass balance evolution during cement paste hardening

The diagram allows us to isolate and consider various aspects of the hardening and strengthening of cement compositions. In particular, a joint analysis of the variation of the capillary and gel components allows us to evaluate the nature and intensity of formation of the porosity of the hardening material, which, in accordance with the “gel-space” concept [2], opens a new pathway to the evaluation of the strength.

Additionally, the diagram offers indirect, but practically full information on the development of the electricity-conducting properties of the material during hardening. Since the gel and non-evaporable components of the structured water conduct electricity to a very limited extent, or not at all, the transfer of electric charges occurs only in capillary water. Therefore, the variation in m_L in Fig. 1 uniquely determines the decrease in electric conductivity (or the increase in electric resistivity) in the hardening process.

Conclusions

The joint analysis of the mass component development kinetics of structured water and the interaction of these components opens new possibilities for the analysis of structure formation and hardening of cement-concrete compositions. In particular, this allows one to study the formation of porosity and hardening, the development of electric conductivity properties etc.

References

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