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Thermodynamic properties of Portland cement hydrates in the system $CaO–Al_2O_3–SiO_2–CaSO_4–CaCO_3–H_2O$

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Abstract

A database is presented for commonly-encountered cement substances including C–S–H, $Ca(OH)_2$, selected AFm, AFt and hydrogarnet compositions as well as solid solutions. The AFm compositions include strätlingite. The data were obtained for the most part from experiment and many of the predicted reactions were confirmed by focussed experiments. The temperature-dependence of the thermodynamic data for the above phases, determined partly from experiment and partly from thermodynamic estimations, are also tabulated in the range 1 °C to 99 °C. Relative to previous databases, sulfate AFm is shown to have a definite range of stability range at 25 °C thus removing long-standing doubts about its stability in normal hydrated cement pastes. Carbonate is shown to interact strongly with stabilisation of AFm across a broad range of temperatures and, at low temperatures, to substitute into AFt. The new database enables the ultimate hydrate mineralogy to be calculated from chemistry: most solid assemblages, the persistence of C–S–H apart, correspond closely to equilibrium. This realisation means that hydrate assemblages can be controlled. The development of a thermodynamic approach also enables a fresh look at how mineralogical changes occur in response to environmentally-conditioned reactions; several papers showing applications are cited.

Keywords: Thermodynamics; Thermodynamic data; AFm; AFt; Hydrogarnet; Ettringite; Stratlingite; Phase relations

1. Introduction

One of the unsolved problems in the application of Portland cement is to quantify the performance lifetimes of concrete constructions. Quantification is important to evaluate the performance of nuclear waste containments and, increasingly, long-lived infrastructure developments, where quantification has failed to keep pace with the expectation of stakeholders.

Although we have a wealth of empirical evidence on the performance of historic concretes, information on their formulation, emplacement and exposure history is often incomplete and, moreover, the nature of cements supplied today will almost certainly have changed since the original construction. Empirical studies and historic examples have however yielded much useful *qualitative* information on the aggressivity of various service environments. Numerous tests and test methods have been used as indicators of durability but they do not yield generic conclusions and their predictive capabilities are limited. As a consequence, designers of long-lived constructions have at present to rely on perceived wisdom, as interpreted by experts and incorporated into codes of practice.

The changing nature of cements is also of concern. Cement producers are under pressure to lower the specific energy requirements of cement production and reduce gaseous emissions. These goals are presently addressed by a combination of methods; partly by optimisation of process technology, including the use of alternative fuels and raw materials (the impacts of which are beyond the scope of this study), and partly by reliance on supplementary cement materials to lessen the need for energy-rich cement. Although the use of supplementary materials is generally regarded as beneficial in terms of strength and durability as, for example, highlighted by developments in

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cement and concrete standards, long term performance is not fully understood. Supplementary materials presently in use include industrial by-products such as slag, fly ash, silica fume, etc. as well as natural materials such as ground limestone, natural pozzolanic and semi-synthetic pozzolans such as metakaolin. Each of these materials has a complex but distinctive chemistry, mineralogy and granulometry. Moreover, each type of material ranges in composition and performance. Studies of their behaviour in blended cements under controlled conditions are confined to selected compositions and short term (1–5 years) laboratory measurements, perhaps supplemented by observations on actual constructions, for which conditions may not be well controlled.

The complexity of blended cement systems and the wide-ranging nature of supplementary cementing materials has meant that guesses – sometimes well informed – have to be made at the outset about what aspects of behaviour should be studied. But the number and complexity of the resulting systems are such that results are often confined to measurement of a few of the many parameters affecting performance. Arguably the most serious question arising from the results of empirical testing is how to extend or extrapolate the results to other compositions and formulations, or to conditions other than those measured, or both. At present we cannot address these issues, except qualitatively.

If quantification of performance is to be achieved, a new paradigm is needed and a key to the development of a successful paradigm must be to concentrate on *generic* approaches. Thermodynamics provides a consistent framework for the analysis of complex systems. Given an adequate database to support calculations, its strength lies in its generic nature; user-defined compositions and conditions can be selected for calculation. This realisation is not new although previous attempts to apply thermodynamics have had only limited success owing partly to deficiencies in the database to enable calculations. In this presentation we concentrate on development of the database.

From an industrial point of view it could be argued that thermodynamic approaches to cement durability are too theoretical and the calculations too difficult to perform. However, the latter is no longer true: geochemists, faced by similar problems of treating complex systems, have developed and validated computer codes capable of being implemented on a PC. Many reliable code packages are available in the public domain. Furthermore codes can be coupled to fluid mass transport modelling modules; in this case, thermodynamic datasets supply important *physical* properties, for example, molar volumes of solid and liquid phases including solid solutions.

Thermodynamics is most readily applied to isochemical systems, i.e., to systems having a constant composition, whereas many cement deterioration reactions involve transport of species into or out of the matrix (or both). In computer-based calculations, such processes also enable more complex conditions to be imposed on the system.

We do not argue that the primary output achieved by application of thermodynamic methods necessarily enables the durability and performance of cements and concretes to be quantified. But we argue that, in the search for quantification, a sound understanding of cement paste mineralogy, and of the ability to calculate features and processes arising from the interaction of cement with potentially aggressive agents introduced from the environment, together with additional possibilities for calculating physical functions and the introduction of kinetic variables, constitutes a great step forward. Other necessary links to develop integrated models of cement performance will be anticipated in discussion.

2. Historical development of cement databases of thermodynamic properties

A thermodynamic database will include many substances for which standard compilations already provide adequate data: it is not necessary to start totally afresh. For example, the thermodynamic properties of water and of many aqueous ions and complexes are well known. Database development focussing on cements is therefore mainly concerned with the properties of solids that are abundant in cements but uncommon or absent in nature. Thus a comprehensive database can be compiled by focussing on relatively few substances.

After years of development, Babushkin et al. published the first reasonably comprehensive compilation of thermodynamic data for cement substances. Their book [1] also gives numerous application examples but, as these are pre-computer, the examples selected for calculation tend to be rather simplistic and at first sight, do not afford significant advance over empirical conclusions. However, a serious problem is that referenced data in this compilation have proved difficult if not impossible to trace to source.

Other databases adding to our knowledge of cement substances have been produced subsequently, e.g., by Atkins et al. [2,3], Damidot [4], Reardon [5,6], Lothenbach and Winnefeld [7], by the Lawrence Livermore National Laboratory [8] and by ANDRA, the French National Agency for Radioactive Waste Management [9]. Studies of phase equilibria, cited subsequently in the text, have also added data on the thermodynamic properties of specific substances.

3. Experimental

A focussed programme of data acquisition was undertaken. This involved synthesis, characterisation, analysis and data integration. New data were obtained through synthesis of phase pure substances with subsequent solubility measurements.

3.1. Analytical procedures

Cement hydrates are generally very sensitive to decomposition by carbonation. Therefore many syntheses and solubility experiments must be performed under N_2 atmosphere to minimize access of atmospheric CO_2. The synthesised solids, aged and stored in inert HDPE or PTFE ware, have been vacuum-filtered with Whatman 540 filter paper and washed several times with ultrapure degassed water to remove alkalis, if present. Subsequently the solids were dried over saturated $CaCl_2$ solution at 37% R.H. for 2 weeks.

Mineralogical examination of the dried solid was made by X-ray diffractometry (XRD) using a PANALYTICAL X'PERT PRO