Extracting kinetic parameters from penetration resistance measurements

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ABSTRACT

ASTM C403 penetration-resistance data are typically fitted with exponential or power functions. Given that the forms of these functions are suggested by either first-order or general-order reaction kinetics, this paper explores applications of kinetics-based interpretations of penetration-resistance data. Data effectively fitted with the exponential function display a pattern associated with the output of a first-order reaction, while data effectively fitted with a power function display a pattern associated with the output of a general-order reaction. Curve-fitting parameters contain "apparent" rate constants, useful for obtaining activation energy for setting behavior. The difference between development of mechanical properties such as penetration resistance with time, and the complex chemistry of multi-phase hydration reactions in the first hours after batching is discussed.

1. Introduction

The early-age increase in stiffness over time of cement-based mortars can be monitored in terms of penetration resistance (*PR*) by the ASTM C403 standard test method [1] or similar techniques [2,3]. To establish a meaningful profile C403 requires only that the data consist of at least 6 (time, *PR*) data pairs, fitted with a "satisfactory curve" that "represents the overall development of penetration resistance and includes points before and after the times of initial and final setting." The most common objective of data collection and subsequent analysis is to visually or computationally interpolate the times at which *PR* equals the criteria of 3.5 MPa defined for initial setting, or 27.6 MPa for final setting. For this purpose ASTM permits "hand-fitting a smooth curve through the data," or computer based regression analysis, fitting the data with the power function:

$$PR = c \cdot t^d \tag{1}$$

where PR = Penetration Resistance, i.e, force F required to embed a probe of area A into the mortar to prescribed depth h; c and d are regression coefficients.

Fitting *PR* data with a power function has its origins in manually fitting the data as a linear function on log-log axes, as has been supported by Popovics [4,5], who further recommended a fixed value of 7 for the exponent d. It is often the case, however, that an exponential function provides an equivalent or superior fit to the same data [6,7,8], using Eq. (2):

$$PR = PR_0 \cdot \exp(a \cdot t) \tag{2}$$

where a and PR_0 are regression coefficients (PR_0 is PR at $t = 0$).

When using computer-aided regression techniques for interpolating setting times, the choice between a power or exponential function may simply depend on which yields the higher value of R^2, or perhaps which yields the better fit in the regions of interest. The purpose of this paper, however, is to suggest that beyond interpolation of setting times, functions that effectively model the whole range of data have the potential to provide additional insight to the overall setting process. For example, data effectively fitted with the exponential function display a pattern commonly associated with the output of a first-order chemical reaction, while data better fitted with a power function may display a pattern associated with the output of a general-order reaction. Of perhaps greater utility, useful "apparent" rate constants for *PR* can be extracted from the regression coefficients obtained for both power and exponential functions, in a manner analogous to the rate constants obtained for simpler applications of reaction kinetics. As will be shown, these apparent rate constants can then be used to quantify the effects of

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temperature on setting behavior. A brief background on the reaction kinetics that inspired these analogies is followed by an experimental demonstration of applications.

2. Reaction kinetics applied to setting behavior

2.1. General

At the onset, there are significant challenges in applying the principles of chemical kinetics to the development of mechanical properties, such as strength or penetration resistance, in paste, mortar, or concrete. First of all, what is commonly termed "hydration" is a series of chemical and physical reactions initiating at different times, proceeding at different rates, and changing with time, is response to temperature, available moisture, and transport processes, with behavior that is far from that of an ideal gas or a dilute solution [9,10,11,12]. Beyond the complexity of the chemical processes under the umbrella term of "hydration," is the subsequently complex linkage between hydration and the development of macro-mechanical properties as growth of micro-structure binds paste and aggregates as a function of time or degree of hydration [13,14,15,16]. When attempting to track progress of the actual chemical reactions by monitoring mechanical properties (instead of measuring masses or volumes of reaction products), one may schematically propose a chain-of-reactions as follows:

$$\text{Chemical–Physical–Mechanical Process} \overset{k(T)}{\rightarrow} \text{Penetration Resistance}(P) \tag{3}$$
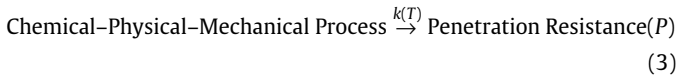
where $k(T)$ is a "rate constant" that quantifies the apparent effect of temperature on the rate of development of the measured macro-property.

For present purposes the "Chemical–Physical–Mechanical process" in Eq. (3) comprehensively includes chemical and physical aspects of the formation of hydration products and their mechanical assembly, as manifested by the evolution of mechanical properties over time. The general, qualitative philosophy of Eq. (3) is imprecise yet applicable to many physical, chemical, and biological systems [17,18,19,20], and is the underlying assumption in application of the maturity method in concrete technology for predicting compressive or flexural strength development, and more recently for predicting setting behavior as characterized by penetration resistance [13,21,22,23].

More specifically, researchers and practitioners have borrowed directly from the fundamental principles of kinetics of simpler chemical systems to predict development of concrete compressive strength [21,24,25,26,27]. A classic example is the use of the Arrhenius equation, based on Maxwell and Boltzmann distribution for ideal gases and dilute solutions [28,29], which is the fundamental core of the widely-used FHP maturity method [21] and ASTM C1074 [30] for predicting concrete strength as a function of temperature. But in each of these cases kinetics has provided a background and functional forms that must be augmented with empirical observations to provide the desired solution. In this paper the authors have adopted functional forms derived from the kinetics of homogeneous chemical reactions that can be used to fit PR data.

2.2. Kinetics of a homogeneous chemical reaction

Consider a generic chemical reaction with gases or dilute solutions where reactants A and B form products C and D in accordance
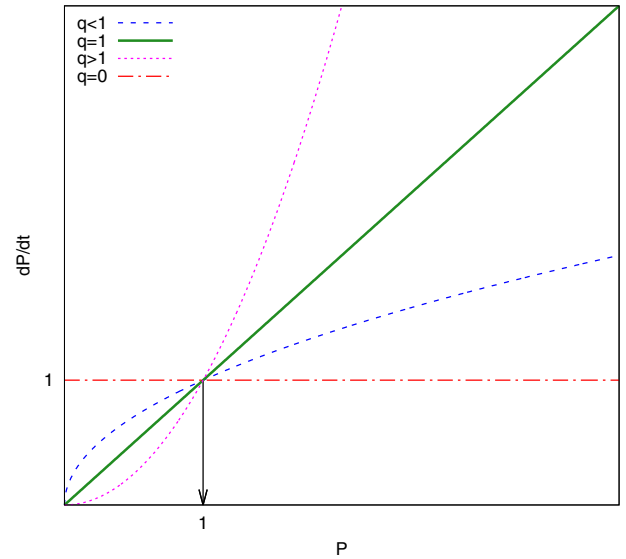

Fig. 1. dP/dt with P for various q (A zeroth-order ($q = 0$) reaction has a constant rate of output-development with time [not necessarily constrained to passing through the point $(1, 1)$]. For a first-order reaction ($q = 1$) the rate increases linearly with the value of $P(t)$, with constant acceleration of output-development. For values of q above or below 1, acceleration of output-development increases or decreases, respectively.)

with $aA + bB \rightarrow cC + dD$. The rate at which the concentration of C changes with time is given by [29]:

$$\frac{d[C]}{dt} = k(T)[A]^m[B]^n \tag{4}$$

where reactants and products are expressed as their concentrations in units such as mol/L, $d[C]/dt$ is the rate of change of concentration of product C in units such as mol/L/h, and $k(T)$ is the rate constant in units of $L^{m+n-1}/mol^{m+n-1}/h$. By monitoring consumption of reactants and formation of products of this chemical process over time and at various temperatures, one can determine k and how it is influenced by temperature [29]. When such reaction occurs within a single phase (homogeneous), depending only on interactions between the reactants, and unlimited by supply of reactants or space to store products, the rate of development of output P over time t is given by the general kinetic expression:

$$\frac{dP(t)}{dt} = kP(t)^q \tag{5}$$

where k is again the rate constant, and the exponent q is called the "order of kinetics" [29]. The term "order of kinetics" (or order of reaction) is characteristic of the nature of the reaction mechanism, as schematically illustrated in Fig. 1. Rates would be expected to continue in accordance with reaction order until either the availability of reactants or the capacity to store or subsequently consume the products limits the reaction, or the nature of the reaction mechanism itself otherwise changes.

2.3. Application of homogeneous kinetics model to setting behavior

Application of this kinetic model to setting behavior requires exploration of the hypothesis that penetration resistance over time (in units of pressure) can be computationally simulated as the output of a simple chemical reaction where the only variables are rate constant, k, and order of reaction q. To test this hypothesis, general