[Review]

Application of the Arrhenius Equation in Geotechnical Engineering

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The reliable measurement of geotechnical properties in cold regions should account for their fluctuations with temperature. The objective of this paper is to introduce a chemical model based on the Arrhenius equation that can predict the properties of materials as their temperature changes. The model can monitor phases and reaction rates as they change with temperature. It has been already applied in the fields of geology, construction, chemistry, materials engineering, and food science. The application of the Arrhenius equation requires a reliable estimate of the activation energy. Therefore, this study also demonstrates several methods for evaluating activation energy in different contexts through summaries and reviews of previous research related to the Arrhenius equation. This paper may be of wide use in obtaining temperature-dependent parameters in geotechnical engineering.

Key words: activation energy, arrhenius equation, geotechnical engineering, phase change, temperature

Introduction

The establishment of a reliable rail link between Europe and Asia has effected notable economic stimulation through improved transportation. The northerly latitudes, including those of the Korean Peninsula (33°-43° N), can show continuously low temperatures even in daytime. At low temperature, soil becomes dense because there is more pore water in the soil, and the soil is also less porous. Andersland and Ladanyi (1994) describe frozen soil as a class of soil, and various researchers have sought to characterize frozen soil. Isaksen et al. (2001) suggested the importance of an active layer after measuring temperature depth profiles through soil. Harris et al. (2003), Humlum et al. (2003), and Rachlewicz and Szczucimski (2008) tried to distinguish frozen layers by measuring long-term temperature data. Invasive methods are limited in that they must penetrate the stiff soil, and non-invasive geophysical methods have been used to examine frozen soil. Gibas et al. (2005) proposed an electrical resistivity survey to detect layers from measured resistivity profiles. Westermann et al. (2010) used Ground Penetration Radar to estimate sub-surface properties. However, the practical use of these techniques has mostly been limited to conditions above $0°C$, and measuring frozen soil in winter remains difficult. Experimental and numerical studies should be performed under winter conditions to determine reliable design parameters.

The Arctic and Antarctic are representative areas consisting of frozen soil that can have similar strength to rock. In such cold regions, penetration tests of strength and other properties are hampered by the difficult conditions. How-

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ever, it is possible to predict the design parameters of cold materials using data measured under non-freezing conditions. Predictions can be made owing to the relationship between the products and reactants of phase changes due to temperature. The Arrhenius equation is the appropriate model for predicting parameters according to phase changes, and it can be used to estimate the properties of materials as temperature and energy change (Amasaki et al., 2000; Galwey and Brown, 2002).

This paper introduces the Arrhenius equation and its use to estimate parameters as temperature varies. The application of the Arrhenius equation in various fields is also examined. Among the equation's input values, the activation energy denotes the energy required to effect a change of phase. The accurate estimation of activation energy is important. Therefore, the method of determining the activation energy is also addressed. Finally, the possibility of using the technique in geotechnical engineering is explored.

Arrhenius equation

The Arrhenius equation, suggested by Svante Arrhenius in 1889, is based on the van't Hoff equation, and it was initially applied to the temperature-dependence of reaction rates. Even though the apparently simple equation is based on the empirical relationship between temperature change and reaction rate, it provides remarkably accurate predictions.

Reacting molecules need to collide with a certain energy in order to react, and their velocity is proportional to the energy of collision. Therefore, temperature, through its effect on molecular velocities, greatly affects the reaction rate. Other factors that influence the rate of a reaction include the type of reaction, the effect of any catalysis, and the reactants' concentrations. Among these factors, this paper focuses on the effects of temperature with regard to phase changes.

Morrison and Boyd (1978) suggested that the reaction rate (R) is the product of the collision frequency (C), an energy factor (E), and an orientation factor (O), as shown in equation (1). The energy factor relates to the energy of a collision being sufficient to perform the reaction, and the orientation factor is related to the probability of collision,
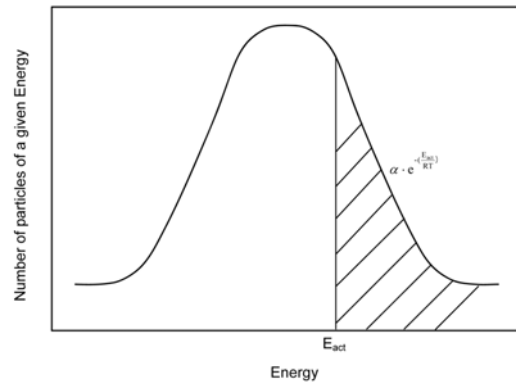

Fig. 1. Gaussian curve of the distribution of energy under ideal conditions (Koerner et al., 1992). E_{act} denotes the activation energy.

as follows:

$$R = C \cdot E \cdot O \tag{1}$$

The collision frequency depends on the pressure, volume, and concentration of the interacting species. The energy factor is influenced by the activation energy and the energy distribution of collisions. The orientation factor accounts for the effect of the relative orientation of the molecules at the time of collision (Koerner et al., 1992).

Maxwell defined the activation energy for an ideal gas in 1852 using a Gaussian curve as the basis for a statistical approach (Fig. 1). The curve of activation energy in Fig. 1 is of exponential form, and thus the energy factor (E) in equation (1) is suggested to be the exponential term in the Arrhenius equation. The other parameters, collision frequency and orientation factor, are combined in the constant A. Finally, equation (1) can be re-expressed as equation (2), the Arrhenius equation:

$$K = A \cdot e^{-\left(\frac{E_{act}}{RT}\right)} \tag{2}$$

where k is the final reactant, A is constant, E_{act} is the activation energy (kJ mol^{-1}), T is absolute temperature (K), and R is the gas constant (8.314 J K^{-1} mol^{-1}).

Application of the Arrhenius equation

The Arrhenius equation shows that the reaction rate (as

expressed by k) depends on the temperature. Therefore, it can be applied to predict the effects of temperature changes. Taking the natural logarithm of equation (2) gives equation (3), which expresses a linear relationship (with slope $-E_{act}/R$) between $1/T$ and $\ln k$, as follows:

$$\ln K = \left(-\frac{E_{act}}{R}\frac{1}{T}\right) + \ln A \qquad (3)$$

The activation energy can be estimated by measuring the rate constant at different temperatures: it would be derived from the slope ($-E_{act}/R$) of a plot of $\ln k$ with respect to $1/T$. A simple demonstration using two rate constants, k_1 and k_2, respectively measured at temperatures T_1 and T_2, is as follows:

$$\ln \frac{K_1}{K_2} = \left(-\frac{E_{act}}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (4)$$

Various fields for applying the Arrhenius equation

Previous works regarding the application of the Arrhenius equation are examined in this section. The equation has been widely applied in various fields including chemistry, materials engineering, and civil engineering.

Electrical resistivity change in cold regions (Hochstein, 1967)

Hochstein (1967) used the Arrhenius equation in geotechnical engineering. The electrical resistivity was measured in frozen areas, and the values correlated with soil density and effective stress at various depths. The surface and deep soils showed a temperature disparity owing to their different thermal conductivities.

To estimate the temperature-compensated electrical resistivity with depth, the Arrhenius equation was applied, because the temperature significantly affected the current flow. Equation (3) was used to find the appropriate activation energy at the experimental site by assuming a linear relationship between the electrical resistivity and temperature.

Aging compensation effect (David, 1987)

Aging compensation is applied in chemistry to correct electrical properties that can change with time. David (1987) analyzed aging effects by comparing the changes of

reaction products with temperature. Predictions were made according to the phase change that occurred with temperature. Furthermore, the behaviors of materials were investigated when various other components were added to the reactants; the activation energies were also deduced in each case. The estimated activation energies show a linear relationship between reactivity and temperature with a high coefficient of determination. The study suggested a temperature index (TI), an integrated data set including the calculated activation energies, for providing the trend of activation energy according to the compound.

Strength changes in concrete (Shi and Day, 1993)

This paper investigated the change in concrete strength when various materials were added to the mixture. The general chemical reaction is an exothermic hydration process due to the alkene substrate. The increments of strength were monitored with the Arrhenius equation as the temperature rose during hardening. The activation energy was also determined using the Arrhenius equation. This paper is significant in that it predicts the activation energy according to the concrete's composition.

Food decay (Petrou et al., 2002)

The Arrhenius equation has also been applied to the study of food. Petrou et al. (2002) examined the temperature dependence of food spoiling, and investigated the engineering characteristics of vegetables, pizza, and chicken balls. An interesting finding is that the relationship between reactivity and temperature shows a quadratic relationship, which differs from the linear function shown in Fig. 2. Furthermore, the coefficient of determination was estimated to have a high value close to 1.0. Note that the activation condition is shown to be affected by various environmental conditions such as temperature and food type.

Change in electrical conductivity of lithium in niobic acid (Bachir et al., 2012)

Niobic acid is a solid compound that has been widely used in chemistry and materials engineering. Its electrical conductivity was investigated when the compound was heated from the outside. The change in electrical conduc-
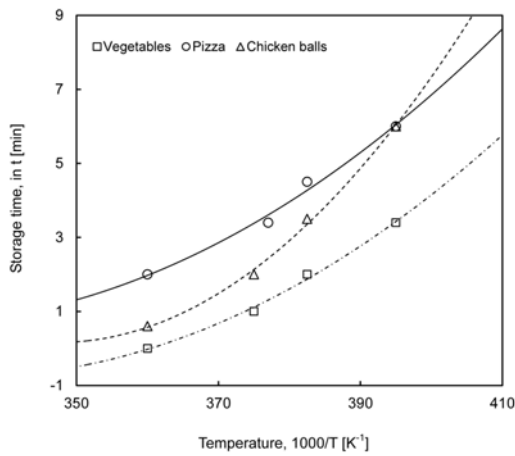
Fig. 2. Relationship between storage time before spoiling and temperature (Petrou et al., 2002). Note that the relationship between storage time (reactivity value) and temperature is not linear, but quadratic.
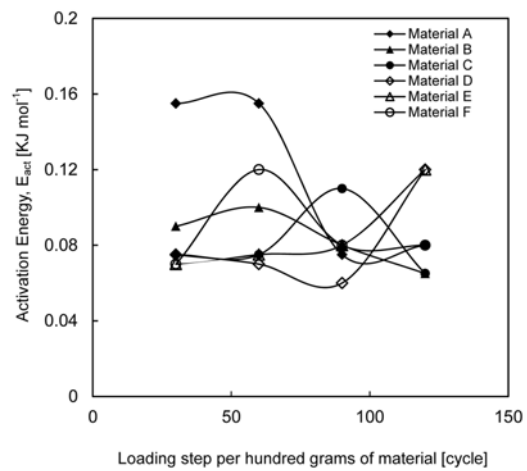

Fig. 3. Variation of activation energy in accordance with loading steps (Hashim et al., 2012). Note that the activation energy shows the diversity according to the dependent value even under the same chemical procedure.

tivity due to heating in the range of 160-300 °C was estimated using the Arrhenius equation. The technique is similar to that used to predict the electrical conductivity of soil, as introduced above in paragraph 1) (Hochstein, 1967). The paper reports that heating increased the electrical conductivity of the solid niobic acid.

Activation energy

The activation energy is the energy threshold above which a chemical reaction occurs; therefore, it is often called a potential barrier for starting the reaction. Note that a number of molecules are required to have at least the activation energy in a reactive system. The Arrhenius equation can optimally predict the characterization of final products under homogeneous reaction conditions (Laidler, 1987). Which reactions occur in a system are determined by various factors including the material properties, reactant concentrations, and the presence of a catalyst. Single uniform activation energy has a limited ability to perfectly reflect complex chemical reactions, even in a one-component system (Anderson, 1967; Redfern, 1970). Therefore, Hunlett (1964) suggested that the Arrhenius equation may be affected by diverse temperature-dependent terms when the relationship between the reaction outcome and temperature is not linear. Hashim et al. (2012) plotted the variation of activation energy with changes to the surrounding

conditions (Fig. 3). The figure shows that the various activation energies, based on the measured electrical conductivity with different loading steps, appear as nonlinear, non-converging curves. Note that an understanding of activation energy is required before the Arrhenius equation can be applied to a given mechanism. Therefore, methods for determining the activation energy are addressed below.

Modification of the Arrhenius equation for specific phase conditions

Polanyi and Wigner (1928) suggested equation (5) to describe solid-state decomposition.

$$\frac{dx}{dt} = \left(-\frac{2\,\nu E}{RT}\right)x_0\exp\left(-\frac{E}{RT}\right) \qquad (5)$$

where dx/dt denotes the reaction rate according to time, x_0 the coefficient of the reaction, and ν the vibration frequency. The other symbols are as defined in equation (3). The vibration frequency generally affects chemical reactions inside or on the surface of crystalloids; Polanyi and Wigner (1928) suggest a value of 1013 Hz. An equation for predicting characterization in the transition range of a chemical process was introduced by Shannon (1964), who used the divided function for distinguishing desorption and loss in the gaseous phase. Young (1966) studied an inter-

esting irreversible reaction under thermo-mechanical conditions, and suggested a new equation assuming zero vibration frequency. Therefore, equation (5) has the vibration frequency replaced with the Planck constant as an input parameter. The Arrhenius equation has been modified for diverse experimental conditions by various researchers. However, it has seen little use in geotechnical engineering owing to the complexity of the specialized terms and the requisite chemical background theory.

Modification of the Arrhenius equation accounting for surrounding conditions

Porokhova et al. (1999) used the Arrhenius equation to obtain temperature-compensated electrical conductivity in the Earth's mantle. The study was conducted to find accurate activation energies giving consideration to the increasing temperature with depth. Therefore, they suggested equation (6), which is a function of the temperature, pressure, and volume changes that occur deep in the earth.

$$K = A \cdot e^{-\left(\frac{\Delta H}{K_S T}\right)} \tag{6}$$

where ΔH is the state function of enthalpy that consists of the activation energy (ΔU) and the changes of both pressure (ΔP) and volume (V). Note that the equation considers more than simply temperature, and includes the state change in its consideration of enthalpy, as shown in Fig. 4. Agreement is shown between the activation energy based on equations (3) and (6) at the surface, because there is little volume or pressure change.

Determination of the activation energy from a nonlinear curve

The activation energy can be deduced from the slope of the relationship between temperature and reaction outcome; however, difficulties arise when attempting to identify the slope of a nonlinear relationship. Hansen and Pedersen (1977) suggested using two equations to describe different temperature ranges as two different linear sections. Their suggested equations were as follows.

$$E = 33500 + 1470\,(20 - T),\ T < 20°C, \tag{7}$$

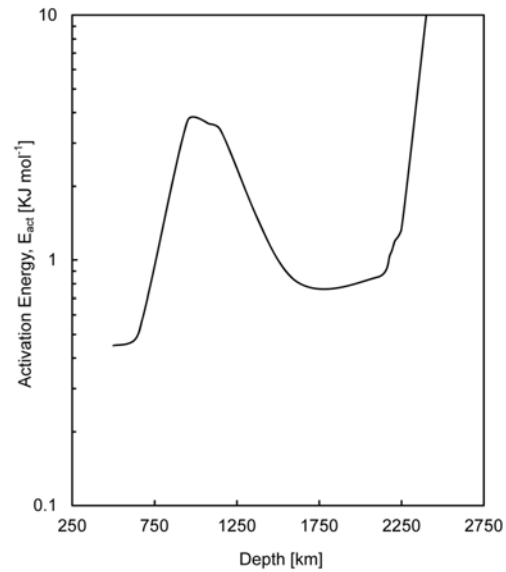$$E = 33500,\ T \geq 20°C$$

Fig. 4. Variation of activation energy with depth below the earth's surface (Porokhova et al., 1999). Note the logarithmic scale of the y-axis. Researchers have suggested a new equation for considering the pressure and volume changes with depth.

where E and T are the activation energy and temperature, respectively.

Statistical method

Haralampu et al. (1985) tried to analyze activation energy by using separated ranges that were linear, divided linear, and nonlinear least-squares regression. The linear and divided linear ranges were analyzed similarly to the method of Hansen and Pedersen (1977). However, they introduced statistical programs (e.g., TROLL, SPS, and MINITAB) for the division into linear curves. The method for nonlinear least-squares regression also used statistical programs. The activation energy was estimated by curve fitting. This study demonstrates that statistical methods can improve activation energy prediction by considering the error ratio.

Factors affecting activation energy

Logsdon (2008) plotted the activation energy according to the electrical spectrum in soil using the Arrhenius equation. The method was similar to that of a previous study; however, this work sought to investigate the factors affect-
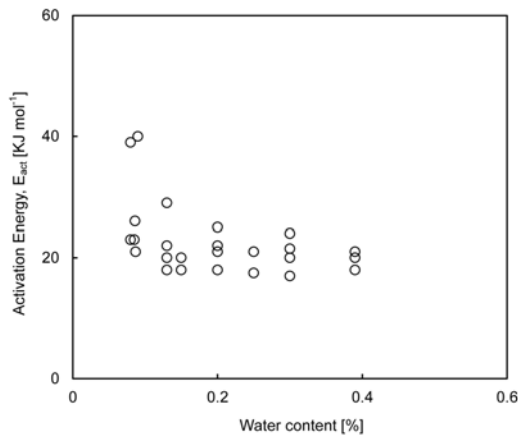
Fig. 5. Relationship between activation energy and water content (after Logsdon, 2008). The results show that activation energy is affected by various environmental factors.

ing the activation energy. The resulting relationship between the water content of soil and activation energy is shown in Fig. 5. The activation energy increased with decreasing water content. In particular, the paper recommends that the charge transfer should be first considered to gather accurate activation energies in the cases of bentonite, montmorillonite, and illite clay particles.

Discussion and conclusion

This work introduces the Arrhenius equation, and examines previous studies of its application in various fields. The activation energy in the Arrhenius equation is an important parameter to predict the products of a reaction system, which greatly depend on the temperature. Therefore, techniques for determining activation energy are also addressed: 1) modification of the equation for suitable consideration of phase conditions; 2) modification of the equation fitting accounting for surrounding conditions; 3) determination of activation energy from nonlinear curves; 4) statistical methods; and 5) factors affecting the activation energy.

Deducing the design parameters of unseasoned soil is difficult, and this complicates construction on it, which might limit the expansion of overseas construction businesses.. In particular, there is little information on the characteristics of frozen soil that is applicable to geotechnical

engineering. The chemical model introduced here can predict the temperature-dependent phase changes, and thus it can be used to estimate the seasonal strength changes in frozen soil that arise owing to the changes of pore water volume that accompany the changing temperature. While the equation requires the determination of activation energy, it may be deduced from dependent variables including water content, void ratio, stress, and other geotechnical properties.

Acknowledgment

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