Journal homepage http://revistas.unitru.edu.pe/index.php/SSMM

SELECCIONES MATEMÁTICAS
Universidad Nacional de Trujillo
ISSN: 2411-1783 (Online)
2025; Vol.12(2):375-382.

Special issue: XII International Congress of Applied and Computational Mathematics

Kinetic evaluation of the Arrhenius equation for artificial ageing of polymers

David Lázaro[*], María González-Alvear[†], Eugenia Morgado[‡], Miguel Á. Jiménez[§] and Angel Cobo[¶]

Received, Abr. 22, 2025; *Accepted, Nov. 03, 2025;* *Published, Dec. 27, 2025*

How to cite this article:
Lázaro, D. et al. *Kinetic evaluation of the Arrhenius equation for artificial ageing of polymers.* Selecciones Matemáticas. 2025;12(2):375–382. https://doi.org/10.17268/sel.mat.2025.02.09

Abstract

Artificial ageing of polymers is a crucial and complex issue, especially considering that critical infrastructures such as nuclear power plants have lifespans varying from 40 to 60 years or even longer. Controlled artificial ageing allows the evaluation of polymer lifetimes while ensuring that their properties are preserved. However, a unified and validated methodology for artificially ageing polymers is still lacking.

One of the most extended methodologies for the artificial ageing of polymers is the Arrhenius methodology. This methodology is based on the application of the Arrhenius equation, which is extensively applied in the study of thermal decomposition reactions. Nevertheless, the Arrhenius methodology requires the estimation of activation energy, and the lack of a unified method introduces variability in results obtained using different methods. Furthermore, the Arrhenius ageing methodology assumes that the kinetic parameters do not change during ageing, meaning that aged and non-aged materials should exhibit the same activation energy.

The present work aims to analyse the hypothesis of unvariable activation energy during ageing. This was investigated using both new and artificially aged PVC samples, evaluating the activation energy through various mathematical models based on thermogravimetric analysis.

Keywords . Ageing of polymers, Arrhenius equation, kinetic parameters, thermogravimetric analysis.

1. Introduction. Nuclear power plants account for around 10% of global electricity generation. In countries such as Spain, the United States, France or Russia, the share of nuclear energy in the electricity generation is approximately 20%, 18%, 62% and 20% respectively. The operational lifetime of nuclear power plants (NPP) has been extended to at least 60 years due to technological innovations and rigorous maintenance practices. However, one of the main concerns regarding lifetime extension is the effect of ageing in the different components of the NPP. In particular, cables are among the most critical components due to their widespread distribution throughout the plant and the difficulty in their replacement.

Cables are typically composed of a copper or aluminium core, with polymer-based insulation and sheath. Within the NPP, several testing techniques have been proposed to diagnose cable health conditions [1]. Nevertheless, these tests mainly focus on the evaluation of naturally aged cables, and fire behaviour is not considered.

To investigate the influence of ageing on polymers, the Arrhenius methodology is widely employed. This accelerated ageing approach exposes polymers to harsher conditions than those encountered in nor-

---

[*] Universidad de Cantabria, Spain. **Correspondence author** (`lazarod@unican.es`).

[†] Universidad de Cantabria, Spain. (`galvearm@unican.es`).

[‡] Consejo de Seguridad Nuclear, Spain. (`eugenia.morgado@csn.es`).

[§] Consejo de Seguridad Nuclear, Spain. (`majg@csn.es`).

[¶] Universidad de Cantabria, Spain. (`acobo@unican.es`).

mal service, such as elevated temperatures, increased radiation dose rates, or other stressors. Although this methodology has certain limitations [2], it is extensively used in the NPP sector. However, as noted in [3], different polymers respond differently to Arrhenius-based ageing, and the methodology should not be applied without first assessing its applicability. This is because the decomposition reactions of many polymers exhibit non-Arrhenius behaviour, reflecting changes in the dominant reaction mechanisms as a function of ageing temperature [4][5][6].

In this work, a methodology is proposed to evaluate the applicability of the Arrhenius ageing approach for a specific polymer. To demonstrate this, the PVC sheath of a cable was analysed using a simultaneous thermal analyser (STA), both before and after artificial thermal ageing. The results reveal the impact of the ageing process on the polymer's decomposition behaviour.

2. Hypothesis and Method. The artificial Arrhenius ageing methodology relies on the assumption that the activation energy does not change due to ageing, meaning that aged and non-aged materials should exhibit the same activation energy. A decomposition reaction produced either by external heating or by natural ageing is defined by the decomposition reaction rate. The reaction rate of decomposition reactions $d\alpha/dt$ is commonly represented by the following equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \tag{2.1}$$

where $f(\alpha)$ is the reaction model dependent on the conversion factor (α).

$$\alpha_i = \frac{m_0 - m_i}{m_0 - m_f}, \tag{2.2}$$

where m_0 is the initial mass before the decomposition reaction, m_f is the mass at the end of the decomposition reaction, and m_i is the mass at a specific time or temperature.

The parameter $k(T)$ is the reaction rate constant, which depends on the temperature T, and is typically assumed to follow the Arrhenius equation:

$$k = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right), \tag{2.3}$$

where A is the pre-exponential factor, E_a the activation energy, and R the universal gas constant.

This equation is also employed in lifetime predictions, which are based on determining the activation energy that quantifies the relationship between temperature and the rate of decomposition.

The Arrhenius ageing methodology considers that natural ageing and artificial ageing have the same mass loss, both following the Arrhenius equation, and thus sharing the same activation energy value:

$$\begin{aligned} k_a &= \left.\frac{d\alpha}{dt}\right|_a = A \cdot \exp\left(-\frac{E_a}{R \cdot T_a}\right), \\ k_s &= \left.\frac{d\alpha}{dt}\right|_s = A \cdot \exp\left(-\frac{E_a}{R \cdot T_s}\right), \end{aligned} \tag{2.4}$$

$$t_a \cdot A \cdot \exp\left(-\frac{E_a}{R \cdot T_a}\right) = t_s \cdot A \cdot \exp\left(-\frac{E_a}{R \cdot T_s}\right), \tag{2.5}$$

$$t_s = t_a \cdot \exp\left[\frac{E_a}{R}\left(\frac{1}{T_s} - \frac{1}{T_a}\right)\right], \tag{2.6}$$

where t_s is the operating time (s), t_a the equivalent ageing time (s), E_a the activation energy (J/mol), R the universal gas constant ($8.314\ J/mol \cdot K$), T_s the operating temperature (K), and T_a the ageing temperature (K).

As mentioned earlier, the validity of this methodology relies on the assumption of a constant activation energy. There is no direct method to measure this value; instead, it is estimated by applying different mathematical models to experimental data in order to determine the parameter that best represents the decomposition reactions obtained in the experiments.

The methodology proposed in this paper to evaluate the validity of the Arrhenius artificial ageing method for polymers is defined by the following steps:

- Preliminary thermogravimetric analysis of the polymer.
- Estimation of the activation energy of non-aged polymer.
- Selection of the artificial ageing protocol:
    - Ageing temperature
    - Ageing time
- Thermogravimetric analysis of the aged polymer.
- Estimation of the activation energy of aged polymer.
- Comparison of activation energies.

The proposed methodology is evaluated in a PVC sheath of a cable in order to evaluate its applicability.

Two main mathematical strategies are employed to study the kinetic parameters of thermal decomposition: analytical methods and curve-fitting optimization methods [7] (see Figure 2.1).

Analytical methods are further divided into model-fitting and model-free approaches. Model-fitting methods assume a specific mathematical form for the reaction model $f(\alpha)$, selected from a set of established solid-state reaction mechanisms. With $f(\alpha)$ fixed, the goal is to determine a single, constant set of kinetic parameters (Ea, A) that best fit the experimental data across the entire reaction. Common implementations include the direct differential [8], Freeman–Carroll [9], and Coats–Redfern [10] methods. A limitation of this approach is that a single reaction model may not adequately describe the entire decomposition reaction. Some studies [8] therefore recommend limiting the conversion degree, α, to an experimental range, typically from $0.01 - 0.11$ at the low limit to 0.67 and 0.98 at the high limit, depending on the material, reaction order, and method.

Model-free methods, in contrast, do not assume a predefined form for the reaction model $f(\alpha)$. Based on the isoconversional principle, they state that, for a constant α, the reaction rate depends only on temperature [11]. These methods require multiple kinetic curves obtained at different heating rates, and their core assumption is that the activation energy remains constant at each degree of conversion. The most widely used isoconversional approaches include the standard isoconversional [12], Ozawa–Flynn–Wall [13], Friedman [14], Vyazovkin [15], and Kissinger–Akahira–Sunose [16] methods. Model-free, non-isoconversional methods employ a single equation to estimate the activation energy and pre-exponential factor. Although these methods are relatively easy to apply, they can be sensitive to data noise [17].

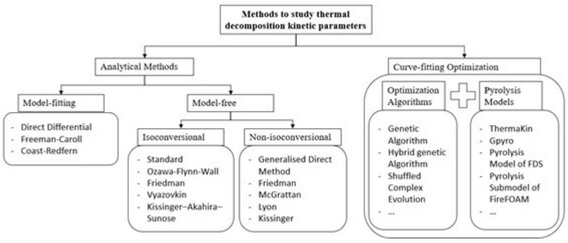

Figure 2.1: Methods developed to calculate kinetic decomposition parameters (adapted from [7]).

In the present work, four isoconversional methods were employed to calculate the activation energy: one differential method, the Friedman equation, and three integral methods, namely the Ozawa–Flynn–Wall equation, the Kissinger–Akahira–Sunose equation, and the Vyazovkin method.

The Friedman equation [14] is obtained by taking the natural logarithm of Equation (2.7), which is derived from the combination of Equations (2.1) and (2.3):

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_\alpha}{R \cdot T_\alpha}\right) \cdot f(\alpha), \tag{2.7}$$

$$\ln\left(\frac{d\alpha}{dt}\right)\bigg|_{\alpha,i} = \ln\big(f(\alpha)A_\alpha\big) - \frac{E_\alpha}{R \cdot T_{\alpha,i}}. \tag{2.8}$$

For a given conversion degree α, the value of E_α is determined from the slope of a plot of $\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i}$ against $1/T_{\alpha,i}$. The index i denotes the temperature programs, and $T_{\alpha,i}$ is the temperature at which the conversion degree α is reached under the ith temperature program.

The integral isoconversional methods are based on the integral form of Equation (2.7):

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \cdot \int_0^t \exp\left(-\frac{E_\alpha}{RT}\right) dt. \tag{2.9}$$

Assuming constant heating rates in the thermogravimetric tests:

$$\beta = \frac{dT}{dt} = \text{constant}. \tag{2.10}$$

This integral form of Equation (2.7) is expressed as:

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E_\alpha}{RT}\right) dT. \tag{2.11}$$

The integral in Equation (2.11) does not have an analytical solution. For this reason, several integral isoconversional methods exist, which differ in the approximations of the temperature integral. Many of these approximations lead to linear regression equations of the general form [8, 9]:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^B}\right) = \text{const} - C \cdot \frac{E_\alpha}{R \cdot T_\alpha}. \tag{2.12}$$

Derived from Equation (2.12), the Ozawa–Flynn–Wall equation [13] has the following form:

$$\ln(\beta_i) = \text{const} - 1.052\frac{E_\alpha}{R \cdot T_\alpha}. \tag{2.13}$$

While Kissinger–Akahira–Sunose equation [16] is given by:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{const} - \frac{E_\alpha}{R \cdot T_\alpha}. \tag{2.14}$$

The Vyazovkin method [15] [18] adopts a different approach, improving accuracy through numerical integration. Considering the integral part as $I[E_\alpha, T_\alpha]$:

$$I[E_\alpha, T_\alpha] = \int_{T_\alpha - \Delta\alpha}^{T_\alpha} \exp\left(-\frac{E_\alpha}{R \cdot T(t)}\right) dT. \tag{2.15}$$

Combining Equations (2.11) and (2.15), we obtain:

$$g(\alpha) = \frac{A}{\beta} \cdot I[E_\alpha, T_\alpha]. \tag{2.16}$$

For different heating rates β_i ($i = 1, \ldots, n$), $g(\alpha)$ remains constant, which leads to:

$$\frac{A_\alpha}{\beta_1} I[E_\alpha, T_{\alpha,1}] = \frac{A_\alpha}{\beta_2} I[E_\alpha, T_{\alpha,2}] = \cdots = \frac{A_\alpha}{\beta_n} I[E_\alpha, T_{\alpha,n}]. \tag{2.17}$$

Nevertheless, since E_α is initially unknown, these equations are not exactly satisfied for a guessed value of E_α. As A_α is constant, it can be removed. To determine the optimal E_α, Vyazovkin defines the function $\Phi(E_\alpha)$, which quantifies the deviation of these ratios from equality:

$$\Phi(E_\alpha) = \sum_{i=1}^{n} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{I[E_\alpha, T_{\alpha,i}]\, \beta_j}{I[E_\alpha, T_{\alpha,j}]\, \beta_i}. \tag{2.18}$$

Minimizing $\Phi(E_\alpha)$ yields the activation energy that best satisfies the isoconversional condition across all heating rates. It should be noted that an exact solution is not possible due to the approximate nature of the Arrhenious-based description of the reaction. Minimization is repeated for each value of α to obtain the dependence of E_α on α. If the temperature is considered to change linearly with time, the function to minimize becomes:

$$\Phi(E_\alpha) = \sum_{i=1}^{n} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]}, \tag{2.19}$$

where

$$J[E_\alpha, T(t_\alpha)] = \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left(-\frac{E_\alpha}{R \cdot T(t)}\right) dt. \tag{2.20}$$

3. Results. As defined in the methodology, thermogravimetric analysis (TGA) of the non-aged polymer was performed to analyse the decomposition reactions and to estimate the activation energy using different mathematical models.

The experiments were carried out with a Netzsch simultaneous thermal analysis (STA) 449 F3 apparatus, which combines thermogravimetry (TG) and differential scanning calorimetry (DSC) in a single test, enabling the simultaneous measurement of mass change and heat flow as a function of temperature. The temperature and balance resolutions are $0.001\,\mathrm{K}$ and $0.1\,\mu\mathrm{g}$, respectively, across the entire weighing range. The DSC enthalpy accuracy is within $\pm 2\%$ for most materials.

An air atmosphere with a gas flow of $40\,\mathrm{mL/min}$ was used to heat the samples from 30 to $800\,^\circ\mathrm{C}$. Heating rates of 5, 10, and $20\,\mathrm{K/min}$ were applied. Two repeatability tests were performed for each sample and heating rate. The results of mass and heat flow are shown in Figure 3.1.

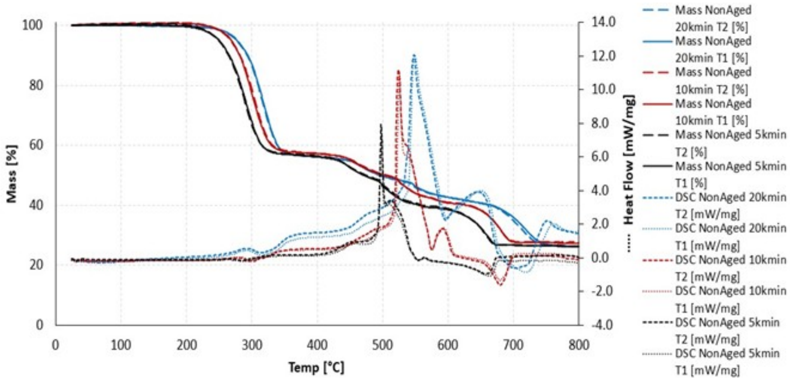

Figure 3.1: Thermogravimetry analysis of non-aged PVC.

For the ageing study, the relevant decomposition reaction is the first one, which occurs between 180 and $380\,^\circ\mathrm{C}$ and, in the case of PVC, is associated with the dehydrochlorination process.

The equations presented in the previous section are employed to estimate the activation energy of the first decomposition reaction for conversion degree values ranging from 0.05 to 0.9, in steps of 0.05.

The activation energy values, represented in Figure 3.2, are obtained from the different mathematical models.

The activation energy varies with α along the decomposition reaction, as well as between the different models employed. All mathematical models exhibit an increasing trend in activation energy values, ranging from approximately $86{,}800\,\mathrm{J/mol}$ at a conversion of 0.05 to a maximum of $160{,}000\,\mathrm{J/mol}$ at $\alpha = 0.9$. Since the Arrhenius ageing methodology requires a single value of the activation energy, the average value of $124{,}832\,\mathrm{J/mol}$ was considered.

The next step is the definition of the ageing protocol. Different ageing temperatures were evaluated considering an ageing time of 7 days, an operating temperature of $40\,^\circ\mathrm{C}$, and the average activation energy value obtained previously. The ageing temperatures analysed using Equation (2.6) were 70, 80, 90, and $100\,^\circ\mathrm{C}$. Figure 3.3 presents the equivalent operating time estimation for these ageing temperatures. Based on these results, an ageing temperature of $100\,^\circ\mathrm{C}$ was selected, corresponding to an artificial ageing equivalent to 43 years.

Once the ageing process is performed, the thermal decomposition of the aged PVC is studied using the STA tests under the same conditions as those employed for the non-aged polymer. Figure 3.4 shows the STA test results for the aged PVC sample. Similar trends in mass loss were observed in the artificially aged sample compared to the non-aged experimental tests.

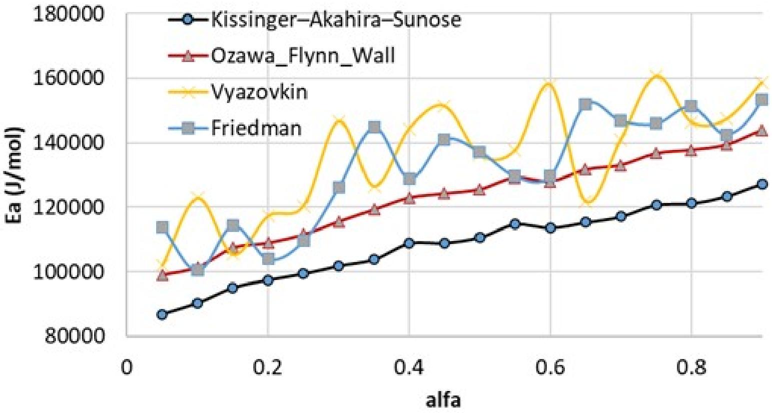

Figure 3.2: Comparison of activation energies of the non-aged sample.

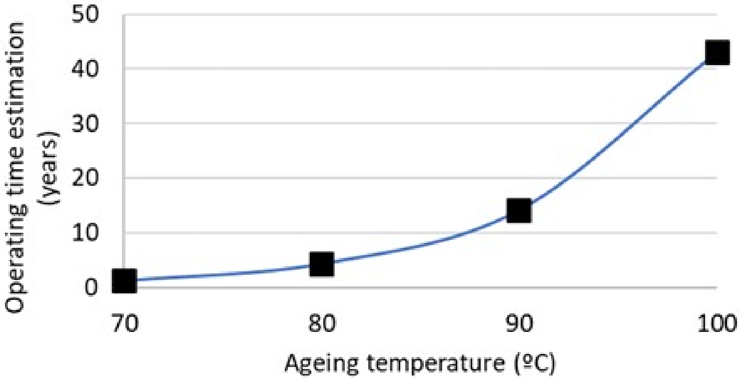

Figure 3.3: Operating time estimation for different ageing temperatures.

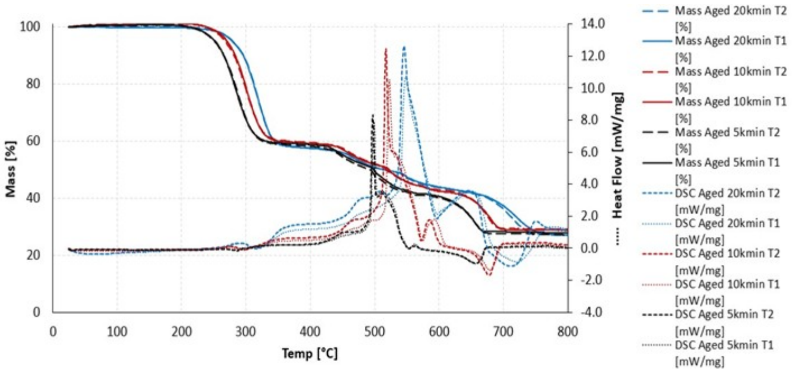

Figure 3.4: Thermogravimetry analysis of aged PVC.

The activation energy curves of the artificially aged sample, obtained from the different mathematical models, are compiled in Figure 3.5. As observed in the calculation of the activation energy for the non-aged sample, there is a wide variation in the estimated activation energy values. Greater discrepancies are observed in the results at the highest conversion values, corresponding to the final part of the decomposition reaction.

Similar to the non-aged sample, all mathematical models show an increasing trend in activation energy values. In this case, these values range from around $83{,}700\,\mathrm{J/mol}$ at $\alpha = 0.05$ to a maximum of $205{,}000\,\mathrm{J/mol}$ at $\alpha = 0.9$. The average of all activation energy values is $118{,}854\,\mathrm{J/mol}$, which is 4.8% lower than the non-aged value.

This lower activation energy in the aged sample is illustrated in Figure 3.6, where activation energies

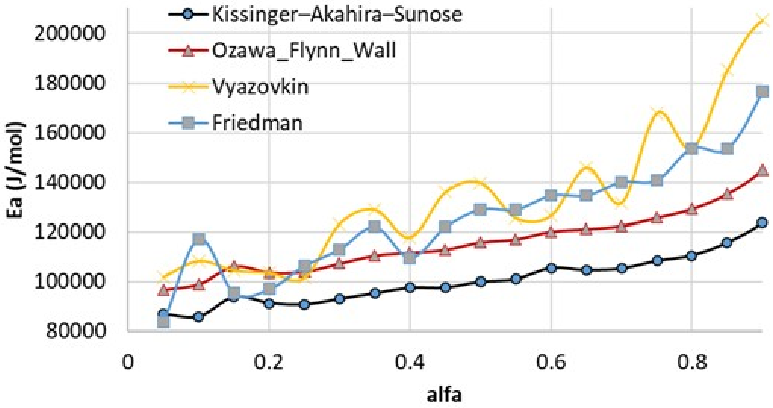

Figure 3.5: Comparison of activation energies of the aged sample.

calculated from the different mathematical models are presented for the non-aged (black lines) and aged (grey lines) samples. The results show that, except for some particular points, the activation energy of the aged samples is lower than that of the non-aged samples.

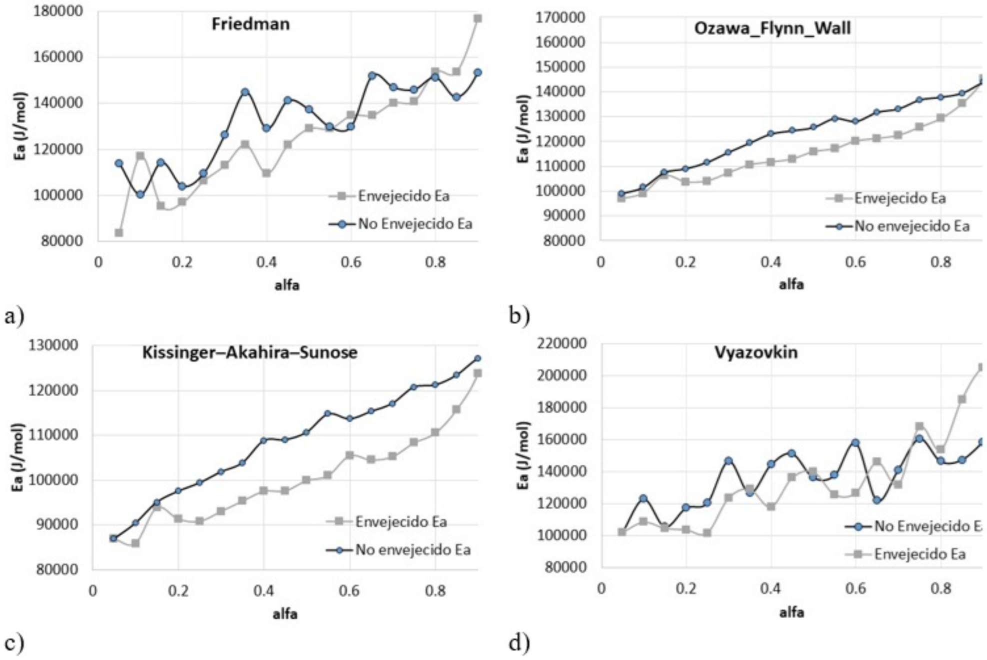

Figure 3.6: Comparison of the activation energy for the non-aged (black) and aged (grey) samples: (a) Friedman model; (b) Ozawa–Flynn–Wall model; (c) Kissinger–Akahira–Sunose model; (d) Vyazovkin model.

4. Conclusions. The present paper presents a methodology to evaluate the adequacy of the artificial thermal ageing method based on the Arrhenius equation. To this end, a comprehensive experimental thermal analysis campaign was conducted on both non-aged and artifitially aged PVC cable sheaths. The methodology is grounded in assessing the hypothesis of constant activation energy during ageing. Given the challenges associated with estimating the activation energy in solid materials, several mathematical models were employed to estimate activation energy. The results reveal significant variation in the activation energy values for the same material depending on the mathematical model used. Nevertheless, all models consistently reflect a trend of increasing activation energy with the conversion factor. Similar behaviour was observed in the thermal decomposition reactions of both non-aged and aged samples during the STA test. Across all models, the aged PVC cable sheaths exhibited slightly lower activation energy, with an average reduction of 4.8%. This deviation represents a measurable departure from the ideal scenario assumed in the

Arrhenius-based artificial thermal ageing method.

Author Contributions. The formal analysis, research, and writing – original draft preparation were completed by David Lázaro, María Gonzalez-Alvear, Eugenia Morgado, Miguel Á. Jimenez, and Ángel Cobo. All authors have read and agreed to the published version of the manuscript.

Acknowledgements. The authors would like to thank the Consejo de Seguridad Nuclear for their cooperation and co-financing of the project "Análisis de modelos numéricos y experimentales para la investigación de incendios en centrales nucleares (FIRENUC)", as well as for their support of the research project SUBV-18/2022 "Validación, calibración y aplicación de modelos de propagación de incendios en escenarios reales de Centrales Nucleares (NUCLEVS)".

ORCID and License

David Lázaro https://orcid.org/0000-0002-8150-4838
María González-Alvear https://orcid.org/0009-0005-2316-6753
Eugenia Morgado https://orcid.org/0009-0008-2484-9312
Miguel Á. Jiménez https://orcid.org/0000-0001-7680-4855
Angel Cobo https://orcid.org/0000-0003-2929-2003

References

[1] IAEA Nuclear Energy Series No. NP-T-3.24 Handbook on Ageing Management for Nuclear Power Plants, Vienna; 2017.
[2] Celina M, Clough RL, Gillen KT. Limitations of the Arrhenius Methododolgy. Albuquerque, NM, and Livermore, CA: Sandia National Laboratories; 1998.
[3] Celina M, Gillen K. Nuclear Power Plant Cable Materials: Review of Qualification and Currently Available Aging Data for Margin Assessments in Cable Performance. SAND2013-2388; 2013.
[4] Gillen K, Bernstein R, Celina M. Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials. Polym. Degrad. Stab. 2005; 87:335–346.
[5] Gillen K, Celina M, Bernstein R. Validation of improved methods for predicting long-term elastomeric seal lifetimes from compression stress-relaxation and oxygen consumption techniques. Polym. Degrad. Stab. 2003; 82:25–35.
[6] Gillen K, Bernstein R, Derzon D. Evidence of non-Arrhenius behavior from laboratory aging and 24-year field aging of polychloroprene rubber materials. Polym, Degrad. Stab. 2005; 87(1):57–67.
[7] Witkowski A, Stec A, Hull T. Chapter 7. Thermal Decomposition of Polymeric Materials. SFPE Handbook of Fire Protection Engineering, 5th ed. New York, USA, Springer; 2016. p. 1-3493.
[8] Sharp J, Wentworth S. Kinetic analysis of thermogravimetric data. Anal. Chem. 1969; 41(14):2060–2062.
[9] Freeman E, Carroll B. The application of thermoanalytical techniques to reaction kinetics. The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. J. Phys. Chem. 1958; 62(4):394–397.
[10] Coats A, Redfern J. Kinetic parameters from thermogravimetric data. Nature. 1964; 201:68-69 https://doi.org/10.1038/201068a0.
[11] Šimon P. Isoconversional methods: Fundamentals, meaning and application. J. Therm. Anal. Calorim. 2004; 76(1):123–132.
[12] Vyazovkin S. Computational aspects of kinetics analysis. Part C. The ICTAC Kinetic Project – the light at the end of the tunnel?. Thermochimica Acta. 2000; 355:155-163.
[13] Flynn F, Wall J. A quick, direct method for the determination of activation energy from thermogravimetric data. Polym. Lett. 1966; 4(5):323-328. https://doi-org/10.1002/pol.1966.110040504
[14] Friedman H. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. J. Polym. Sci. Part C Polym. Symp. 1964; 6(1):183–195.
[15] Vyazovkin S. Modification of the integral isoconversional method to account for variation in the activation energy. J. Comput. Chem. 2001; 22(2):178–183.
[16] Akahira T, Sunose T. Method of determining activation deterioration constant of electrical insulating materials. Research Report Chiba Institute of Technology (Science Technology); 1971.
[17] Matala A, Lautenberger C, Hostikka S. Generalized direct method for pyrolysis kinetic parameter estimation and comparison to existing methods. J. Fire Sci. 2012; 30(4):339-356.
[18] Vyazovkin S, Burnham A.K, Criado J.M, Pérez-Maquedac L.A, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochimica Acta. 2011; 520(1-2):1-19.