

*Full Length Research Paper*

# Use of finite element method as a simulation technique for bioremediation of naphthalene, anthracene and pyrene contaminated soil in a fixed bed reactor

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**In this work, the finite element method was applied to solve one-dimensional advective-dispersive solute transport model with linear equilibrium sorption and first-order degradation. This mathematical approach was adopted to adequately predict the effluent concentrations and breakthrough profiles of naphthalene, anthracene and pyrene. Simulation results showed that the concentrations of naphthalene, anthracene and pyrene within a contact period of 49 days, decreased in the direction of flow from 100 mg/l at the surface to zero at 9 cm subsurface depth. The residual concentrations of naphthalene, anthracene and pyrene were found to be 0, 35.79 and 0% respectively by the 49th day of exposure. The theoretical predictions when compared with actual experimental results from the soil column showed an average deviation of 3.92%, an indication of a reasonable agreement between the model and data from experiment. The finite element method has been found to be satisfactory as a predictive tool to show the distribution of the contaminant solutes. This is significant as it displays the capacity of ascertaining the behaviour of these contaminants over long spatial and temporal scales and predicting the extent of bioremediation of the contaminated sites.**

**Key words:** Naphthalene, anthracene, pyrene, finite element, predictive tool, bioremediation.

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are important pollutants found in air, soil and sediments (Da Silva et al., 2003). They and their derivatives are widespread products of incomplete combustion of organic materials arising, from natural combustion such as forest fires and volcanic eruptions (Mrozik et al., 2003). In recent times, the major source of PAH pollution are industrial production, transportation, refuse burning, gasification and plastic waste incineration (Mrozik et al., 2003).

Aromatic hydrocarbons are composed of numerous substances originating from crude oil and their contribution can vary from 4 to 22% depending on substance type (Oleszczuk et al, 2003). PAHs constitute one of the most harmful groups of aromatic hydrocarbons; due to their properties, and they are characterised by their high durability in the environment, thus promoting their tendency to bioaccumulate and thereby reducing their availability for degradation (Oleszczuk et al., 2003).

The technique for selecting efficient design methods

and or parameters depends on the development of realistic models for the mathematical description of the process. Mathematical modelling is an accepted scientific practice, providing the mechanism for comprehensively integrating basic processes and describing a system beyond what can be accomplished using subjective human judgements (Mirbagheri, 2004). It is therefore possible to develop models that better represent the natural system and then use these models in an objective manner to provide a guide for current management practices, generate data, which hitherto have been limited for future research efforts. The data constitute a major source of information for the environmental practitioners in the oil and gas industries who are constantly faced with the problem of petroleum and petroleum product spill.

The modelling of contaminant transport hinges on an understanding of the mechanisms of mass transfer from the solid adsorbed phase to the liquid phase, and contaminant decay (Mirbagheri, 2004; Owabor, 2007). Advection-dispersion phenomena occur in many physical situations including the transfer of heat in fluids, flow through porous media, and the spread of contaminants in fluids and in chemical separation processes (Najafi et al., 2008)

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Various methods have been applied to solve the one-dimensional advection-dispersion equation which describes the flow of contaminant organic solutes within the soil matrix (Pang et al., 2003; Owabor, 2007; Najafi et al., 2008).

In this study the finite element method (FEM) was employed to solve the one-dimensional advection-dispersion transport model with linear sorption equilibrium and first order degradation. The proposed methodology is sensitive to changes in the concentration of contaminant with time as a function of the axial direction of flow. The use of the finite element technique to simulate the concentration with time of naphthalene, anthracene and pyrene in a soil column is with a view to presenting an alternative option for ascertaining the extent of bioremediation of PAH contaminated soils. This will provide a viable solution or management strategy to maintaining the integrity of the environment in the light of the limitations arising from the expensive and cumbersome nature of experimental studies over sufficiently long distances and/or time periods.

**Theoretical framework**

In the development of the dispersion-advection equation, the following assumptions were made:

1. Solute transport in porous media is by diffusion governed by Fick's law.
2. The generalized principle of the conservation of mass.
3. Linear sorption isotherms.
4. The flux of the solute is affected by geochemical reaction (sorption).
5. The pore water velocity of the solute in porous media is constant.
6. Diffusivity coefficients are independent of position in the x-direction.

The one-dimensional advection-dispersion equation proposed by Najafi et al., (2008) was used in this study. The equation describes the transient transport of solutes through a homogenous soil matrix.

**Method of solution**

The governing transport equation (Pang et al., 2003), resolved using the finite element method (FEM) is given by:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - \lambda C \tag{1}$$

The finite element method is a technique in which a given domain is represented as a collection of simple sub domains, called "finite elements", so that it is possible to systematically construct the approximation functions needed in a variational or weighted residual approximation of the solution of a problem over each element (Reddy, 1993 and Chapra et al., 1998).

The finite element method is an element-wise application of the Rayleigh-Ritz or weighted-residual methods. The finite element method differs from the traditional Rayleigh-Ritz, Galerkin, least

squares, collocation, and other weighted-residual methods in the manner in which the approximation functions are constructed. But their difference is responsible for the following three basic features of the finite element method (Reddy, 1993):

1. Division of whole into parts, which allows representation of geometrically complex domains as collections of geometrically simple domains that, enable a systematic derivation of the approximation functions.
2. Derivation of approximation functions over each element; the approximation functions are often algebraic polynomials that are derived using interpolation theory.
3. Assembly of elements, which is based on continuity of the solution and balance of internal fluxes; the assemblage of elements represents a discrete analogue of the original domain, and the associated system of algebraic equations represents a numerical analogue of the mathematical model of the problem being analyzed.

The finite element method overcomes the disadvantage of the traditional variation method by providing a systematic procedure for the derivation of the approximation functions over sub-regions of the domain (Desai and Abel, 1972; Reddy, 1993).

Since the conditions considered in this work are represented by linear sorption equilibria, the resultant set of partial differential equations (PDEs) were solved numerically by first reducing them to a set of ordinary differential equations (ODEs) using the FEM of solution. The finite element solution of the model is described by Equations 2 - 10.

Initial conditions:

$$C(0,0) = C_i$$

$$C(0,t) = C_i \quad 7 \leq t \leq 63$$

$$C(x,0) = 0 \quad 0.01 \leq x \leq 0.09$$

Boundary condition:

$$D \frac{dC}{dx} \Big|_{x=L} = 0$$

To develop the weak formulation of equation (1), the equation was rearranged and multiplied with the weight function to obtain equation (2):

$$0 = w \left[ D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - R \frac{\partial C}{\partial t} - \lambda C \right] \tag{2}$$

Integrating equation (2) over an element to obtain the weighted-residual equivalent of the equation (1), we have equation (3)

$$0 = \int_{x_e}^{x_{e+1}} w \left[ D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - R \frac{\partial C}{\partial t} - \lambda C \right] dx \tag{3}$$

Integrating equation (3) using the method of integrating-by-parts, we have equation (4)

$$0 = w(x_A) \left( D \frac{dC}{dx} \right)_{x_A} - w(x_B) \left( D \frac{dC}{dx} \right)_{x_B} + \int_{x_B}^{x_A} \left( -Vw \frac{dC}{dx} - D \frac{dw}{dx} \frac{dC}{dx} - Rw \frac{dC}{dt} - \lambda wC \right) dx \tag{4}$$

**Table 1.** Dispersion Coefficient for contaminant PAHs [Owabor, 2007].

PAHs	Dispersion Coefficient, D (m <sup>2</sup> /day)
Naphthalene	8.61E-6
Anthracene	8.59E-6
Pyrene	8.567E-6

Where,  $x_A = x_e$  and  $x_B = x_{e+1}$

$$0 = \int_{x_B}^{x_A} \left( -Ww \frac{dC}{dx} - D \frac{dw}{dx} \frac{dC}{dx} - Rw \frac{dC}{dt} - \lambda w C \right) dx - w(x_A) Q(x_A) - w(x_B) Q(x_B) \tag{5}$$

But the finite element approximation functions were given by:

$$C \approx \sum_j^n C_j^e(t) \psi_j^e(x) \tag{6}$$

$$w = \psi_i^e \tag{7}$$

Substituting equations (6) and (7) into equation (5)

$$0 = \sum_{j=1}^n \int_{x_B}^{x_A} \left( -V \psi_i^e \frac{d\psi_j^e}{dx} - D \frac{d\psi_i^e}{dx} \frac{d\psi_j^e}{dx} - \lambda \psi_i^e \psi_j^e \right) C_j^e(t) dx - \sum_{j=1}^n \int_{x_B}^{x_A} R \psi_i^e \psi_j^e \frac{dC_j^e(t)}{dt} dx - \sum_{j=1}^n \psi_i^e(x_j) Q_j^e \tag{8}$$

The finite element solution of the model was represented as:

$$[K_{ij}^e] \{C_j^e(t)\} - [M_{ij}^e] \left\{ \frac{dC_j^e(t)}{dt} \right\} = \{Q_i^e\} \tag{9}$$

While the assemblage of two-element mesh of the finite element solution of the model was given as:

$$[K] = \begin{pmatrix} \frac{V}{2} \frac{7D}{3h_e} - \frac{2\lambda h_e}{15} & \frac{8D}{3h_e} - \frac{2V}{3} - \frac{\lambda h_e}{15} & \frac{V}{6} - \frac{D}{3h_e} + \frac{\lambda h_e}{30} & 0 & 0 \\ \frac{2V}{3} + \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & -\frac{16D}{3h_e} - \frac{8\lambda h_e}{15} & \frac{8D}{3h_e} - \frac{2V}{3} - \frac{\lambda h_e}{15} & 0 & 0 \\ \frac{\lambda h_e}{30} - \frac{D}{3h_e} + \frac{V}{6} & \frac{2V}{3} + \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & -\frac{14D}{3h_e} - \frac{4\lambda h_e}{15} & \frac{8D}{3h_e} - \frac{2V}{3} - \frac{\lambda h_e}{15} & \frac{V}{6} - \frac{D}{3h_e} + \frac{\lambda h_e}{30} \\ 0 & 0 & \frac{2V}{3} + \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & -\frac{16D}{3h_e} - \frac{8\lambda h_e}{15} & \frac{8D}{3h_e} - \frac{2V}{3} - \frac{\lambda h_e}{15} \\ 0 & 0 & \frac{\lambda h_e}{30} - \frac{D}{3h_e} + \frac{V}{6} & \frac{2V}{3} + \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & -\frac{V}{2} - \frac{7D}{3h_e} - \frac{2\lambda h_e}{15} \end{pmatrix} \tag{10}$$

$$[M] = \begin{pmatrix} \frac{2Rh_e}{15} & \frac{Rh_e}{15} & -\frac{Rh_e}{30} & 0 & 0 \\ \frac{Rh_e}{15} & \frac{8Rh_e}{15} & \frac{Rh_e}{15} & 0 & 0 \\ -\frac{Rh_e}{30} & \frac{Rh_e}{15} & \frac{4Rh_e}{15} & \frac{Rh_e}{15} & -\frac{Rh_e}{30} \\ 0 & 0 & \frac{Rh_e}{15} & \frac{8Rh_e}{15} & \frac{Rh_e}{15} \\ 0 & 0 & -\frac{Rh_e}{30} & \frac{Rh_e}{15} & \frac{2Rh_e}{15} \end{pmatrix} \tag{11}$$

The time approximated solution of the model yields:

$$\{[M]\}\{C\}_s = \{[M] - \Delta t_{s+1} [K]\}\{C\}_{s+1} + \Delta t_{s+1} \{Q\}_{s+1} \tag{12}$$

**Simulation method**

MathCAD was used to simulate the time dependent concentration distribution of the contaminant PAHs in a soil column.

The finite element solution of the model was incorporated into MathCAD software. The parameters in Tables 1 - 3 were used for the simulation of concentration of naphthalene, anthracene and pyrene in the aqueous-soil matrix.

**RESULTS AND DISCUSSIONS**

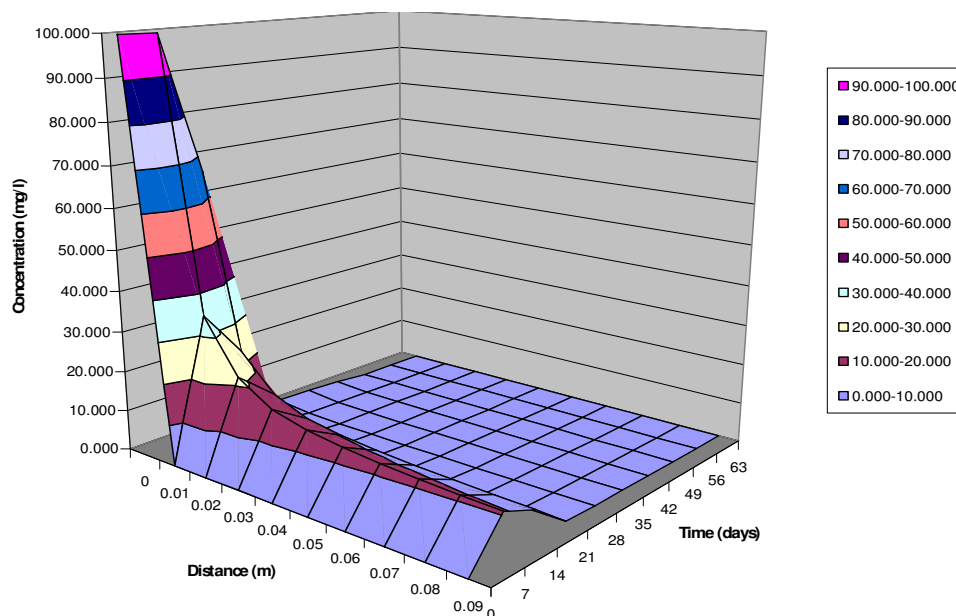
The results of the computation analysis of the modelling equation of the bioremediation of PAH contaminated surface and subsurface soils using the finite element-simulation technique are presented below. The model was applied to simulate the concentrations of naphthalene, anthracene and pyrene in a soil column using the experimental data of Owabor (2007).

Figures 1, 2 and 3 show the variation of concentration of naphthalene, anthracene and pyrene with time and distance respectively. The profiles revealed a rapid and an exponential decay of the contaminant solute from the surface to a subsurface distance of 5 cm. This was closely followed by a gradual decay from a subsurface distance of 6 - 9 cm for naphthalene and pyrene respectively, and from a subsurface distance of 7 - 9 cm for anthracene. The observed pattern of disappearance suggests that naphthalene is removed first followed by pyrene and anthracene. This behaviour can be attributed to the differences in their properties (number of aromatic rings, molecular weight, aqueous solubility, diffusivity in water and soil, resistance to mass transfer) and also the soil characteristics (Oleszczuk et al., 2002; Johnsen et al., 2005; Owabor, 2007). The solubility and diffusivity of these contaminants, promotes diffusive mechanism, facilitates the transport of the compound and enhances their availability in solution for utilization.

Low diffusivities have been observed in the soil when compared to diffusivities in water (Owabor, 2007). This suggests that diffusion in the pores of the soil may be retarded by surface adsorption/desorption effects on soil organic carbon, mineral surfaces and interstitial voids within the micropores and submicropores of the soil particle. The role of soil structure in the effective delivery of air, water and nutrients cannot be overemphasized and hence it is an important factor primarily considered for a successful bioremediation process. The salient characteristics of the soil used to generate the experimental results which aided the resolution of model presented in this study showed that the soil was highly porous with a particle size distribution in the ratio 85:14:1% for sand, clay and silt respectively. The cation exchange capacity of the soil was within the recommended values of 5 cmol/

**Table 2.** First-order degradation constants and Retardation factors for contaminant PAHs (Owabor, 2007).

PAHs	Degradation Constant $\lambda$ (day <sup>-1</sup> )	Retardation factor (R)
Naphthalene	41.76	25.77
Anthracene	20.16	41.62
Pyrene	27.36	35.66



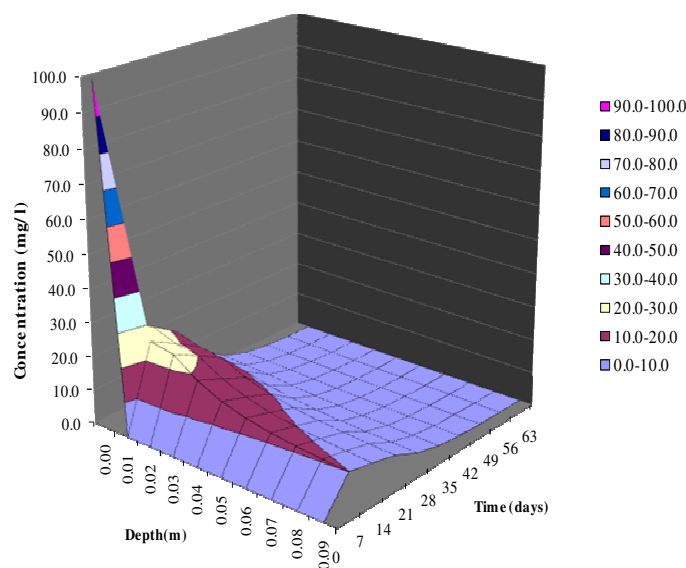
**Figure 1.** Variation of concentration of naphthalene with time and depth.

**Table 3.** Pore-water velocity of soil samples (Owabor, 2007).

Soil sample	V (m/day)
Fine Sand	0.36
Coarse Sand	0.42
Silt Clay	0.31
Clay	0.25

kg for sandy soil low in organic matter (Owabor, 2007). This is especially significant because decaying organic matter shrinks and swells and encourages micro fauna which create or widen openings in the soil thus improving infiltration and aeration.

The profile in Figure 1 show that as the time increases, the concentration of naphthalene decreases from 100 mg/l at the surface to zero by the 49th day of exposure within the soil matrix. Also, the result shows that the concentration of naphthalene decreases in the direction of flow in the subsurface of the soil with the least value at the subsurface distance of 9 cm from the surface of the soil. The residual concentrations of naphthalene at the surface and at a subsurface distance of 9 cm are 0.82 and 0.09 mg/l respectively. Similar trends were observed



**Figure 2.** Variation of concentration of anthracene with time and depth.

for anthracene and pyrene with residual concentrations at the surface and subsurface distance of 9 cm as 0.57, 0.20, 2.26 and 0.51 mg/l respectively.

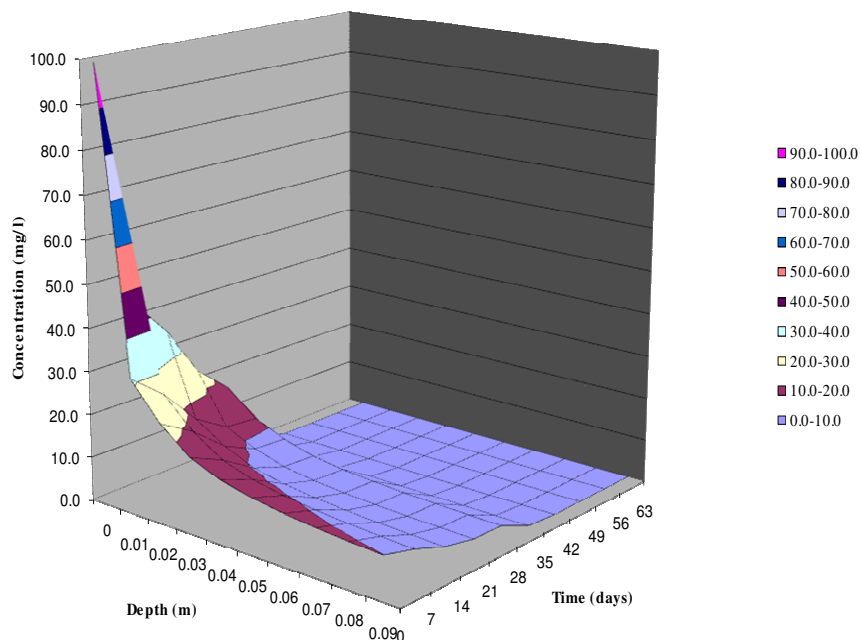


Figure 3. Variation of concentration of pyrene with time and depth.

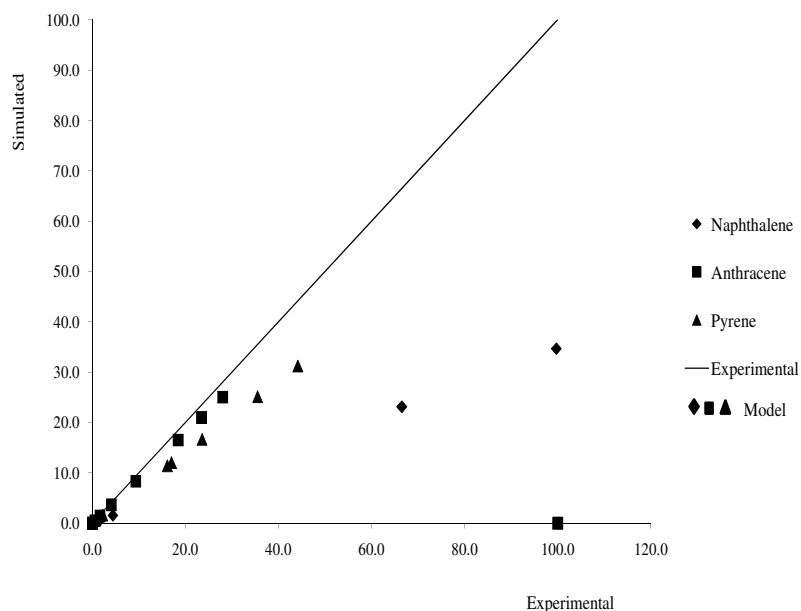


Figure 4. Experimental and Simulated degradation of naphthalene, anthracene and pyrene in soil fixed bed reactor

The marked variation in concentrations between pyrene and anthracene in spite of the fact that pyrene has a higher molecular weight may be attributed to the differences in their structural configuration, the very low solubility of anthracene and the close diffusivity exhibited between anthracene and pyrene. Anthracene has a linear

structure in which the benzene rings are tightly fused together while pyrene has a tetrahedral structure in which the rings are loosely fused. This creates porosity within the interstitial spaces between the rings making it susceptible for microbial attack. The results, therefore, implicates pattern of ring linkage and molecule topology as

factors which could be considered as very important in the study of the polycyclic aromatic hydrocarbon degradation.

The developed model which had a number of variables whose numerical values were independently estimated was validated to assess the variation of the simulated composition of naphthalene, anthracene and pyrene with exposure time within the soil matrix. A comparison of the experimental and simulated results is shown in Figure 4. Generally, the numerical solution of the model for the axial direction of flow of the contaminant solutes gave a reasonable agreement with the experimental data with an average deviation of 3.92%.

### Conclusion

The finite element method has been found to be satisfactory in solving the non-steady state model and can be used to predict the extent of bioremediation of soils contaminated with PAHs. This therefore does not necessitate the need for experimental assay for the time required for the clean-up of soils polluted with PAHs.

This model can also be used to determine the actual movement of contaminant solute within the soil matrix and in the direction of flow in the subsurface of the soil. The results affirm that the microbial utilization of pyrene and anthracene for metabolic activities were greatly limited by their resistance to mass transfer between the fluid phase and the soil matrix arising from their low aqueous solubility. The result confirmed that naphthalene degrades faster in the soil matrix than pyrene and anthracene.

**Nomenclature:**  $C$  ; Concentration (mg/l),  $D$  ; Dispersion coefficient, ( $m^2/day$ ),  $h_e$  ; Height of an element,  $K_{ij}^e$  ; Stiffness matrix,  $M_{ij}^e$  ; Mass matrix,  $R$  ; Retardation factor,  $\lambda$  ; First-order degradation constant (/day),  $V$  ; Pore-water velocity (m/day),  $\psi_i^e$  ; Quadratic Lagrange interpolation functions,  $\bar{x}$  ; Local coordinate,  $w$  ; Weight function,  $\phi$  ; Total porosity,  $t$  ; Time (days),  $x$  ; Distance (m),  $\alpha$  ; Numerical integration scheme,  $\Delta t$  ; Time increment and  $\Omega^e$  ; An element domain.

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