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426.1/B0287/DJB/85/03/22

MAR 26 1985

Susan K. Whatley, Manager
Engineering Analysis and Planning
Chemical Technology Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37830

Dear Ms. Whatley:

SUBJECT: CONTRACT NO. NRC-50-19-03-01, FIN B-0287, ORNL NO. 41-37-54-92-4, "TECHNICAL ASSISTANCE IN GEOCHEMISTRY," FEBRUARY 1985, MONTHLY PROGRESS REPORT

I have reviewed the February monthly progress report dated March 11, 1985. Based on my review, I have the following comments:

Tasks 1, 2, and 3 - BWIP, NNWSI and Salt Geochemical Technical Assistance

° Progress to date is satisfactory.

° I am sending (under seperate cover, and for your information) a copy of our EA comments on Hanford, NNWSI and seven salt sites.

° I will be reviewing the draft topical report on Hanford solubility work. I plan to have comments to you by the week of April 22, 1985.

° I am coordinating a review of the topical report on matrix diffusion with Linda Kovach. According to Jim Blencoe, comments received so far are being incorporated into the current draft. When this has been completed, send us a copy. As soon as the revised draft has been received, Linda will call you to work out a schedule for our review, and finalizing the report.

° Please let me know in the next monthly report, the status of the work being done on brine migration.

Task 4 - Short-term Geochemial Technical Assistance

° Progress to date is satisfactory.

° Attachments 1 and 2 need to be reviewed. We would like to receive comments by April 8, 1985. Please let me know if there are any problems with this deadline.

OFC :WMGT	:	:	:	:	:	:
NAME :DJBrooks;mt	:	:	:	:	:	:
DATE :85/03/	:	:	:	:	:	:

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Task 5 - Project Management

- Progress to date is satisfactory.
- I am returning "Geochemical Aspects of Radioactive Waste Disposal," that I borrowed from your library. Thank you for the loan.
- Please let me know the progress of the draft letter reports on plutonium and americium chemistry that are to be done in support of B0290.

The action taken by this letter is considered to be within the scope of the current contract (NRC-50-19-03-01/FIN B-0287). No changes to costs or delivery of contracted products is authorized. Please notify me immediately if you believe this letter would result in changes to costs or delivery of contracted products.

Sincerely,

Original Signed By

David J. Brooks
Geochemistry Section
Geotechnical Branch
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosures:
As Stated

OFC	WMGT					
NAME	DJBrooks:mt					
DATE	85/03/25					

FY84 Annual

Attachment 1

Letter Report

GEOCHEMICAL SENSITIVITY ANALYSIS

I. RADIOELEMENT SPECIATION

Identification of Conditions and Criteria for Design of Transport Experiments When Radioelement Speciation Must Be Considered in High-Level Waste Repository Risk Assessment

December 1984

M. D. Siegel
Division 6431

K. L. Erickson
Division 1512

D. A. Vopicka
Division 7223

Sandia National Laboratories
Albuquerque, NM 87185

Prepared for
Division of Waste Management
Office of Nuclear Materials Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555

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DRAFT

ATTACHMENT 2

Analysis of Data From Batch Sorption Experiments When Radionuclides Undergo Chemical Speciation Reactions

K. L. Erickson

Introduction

In typical batch sorption experiments fluid-phase compositions are monitored until no statistically significant change appears to occur during some time period, which is usually on the order of several days. The system is then assumed to be at equilibrium. However, some chemical speciation reactions which convert strongly sorbing species to more weakly sorbing species might occur too slowly to be detected during the given time period, but would occur rapidly enough to seriously affect cumulative radionuclide discharges during a regulatory period which is on the order of ten thousand years. A numerical example illustrating these effects is given below, and some basic considerations for designing or evaluating data from batch sorption experiments are described.

Theory

Consider a batch sorption experiment in which a fluid phase containing a given radionuclide Nj of element N is contacted with a solid phase. In the fluid phase, let the radionuclide exist as two chemical species, A_1 and A_2, which undergo the chemical speciation reaction

$$A_1 + \ell L \rightleftharpoons aA_2$$

where L denotes some other fluid-phase constituent, and a and ℓ are stoichiometric coefficients. The corresponding reaction rate expression is

$$r_{A_1} = -\frac{dC_{A_1}}{dt} = k_1 C_{A_1}^{n_1} C_L^{n_L} - k_2 C_{A_2}^{n_2} \qquad (1)$$

where C_{A_1}, C_{A_2}, and C_L are the fluid-phase molar concentrations of species A_1, A_2, and L, respectively; k_1 and k_2 are the forward and reverse reaction rate constants, respectively; the exponents n_1, n_2, and n_L are greater than zero; r_{A_1} denotes the rate of depletion of species A_1, and t denotes time. In most cases, the exponent n_1 in Equation (1) will be unity or greater; C_{A_1}, will be less than 1 molar, and the expression

$$r_{A_1} \approx k^* C_{A_1} \tag{2}$$

will give reaction rates equal to or greater than those obtained from Equation (1). In Equation (2), $k^* = k_1 C_{L_{max}}^{n_L}$, and $C_{L_{max}}^{n_L}$ is the maximum anticipated value of $C_L^{n_L}$.

Let $\bar{C}_{A_1}$ and $\bar{C}_{A_2}$ denote the solid-phase concentrations (mole/kg) due to sorption of species A_1 and A_2, respectively, and let the sorption equilibria for species A_1 be more favorable than those for species A_2. For purposes of illustration, assume that the sorption isotherms can be considered at least approximately linear. Also, since sorption rates, particularly those for physical adsorption and ion exchange, are diffusion-limited, either in the fluid and/or solid phase, a reasonable expression for sorption rates would be of the form

$$\frac{d\bar{C}_{A_i}}{dt} = \rho hs \left(\Gamma_{A_i} C_{A_i} - \bar{C}_{A_i}\right) \tag{3}$$

where h = mass transfer coefficient, cm/day

s = surface area of the solid per unit mass, cm^2/gm

t = time, day

Γ_{A_i} = sorption equilibrium distribution function for species A_i (taken as at least approximately constant), cm^3/gm

ρ = grain density of the solid, gm/cm^3.

Typical half-lives for sorption reactions in laboratory batch experiments are on the order of hours to days. Note that for the case in which sorption rates are limited by diffusion in the solid-phase. C_{A_i} is the average solid-phase concentration at any given time and the quantity $\Gamma_{A_i} C_{A_i}$ is the equilibrium solid phase concentration defined by the isotherm.

If Equation (2) is used to give an upper bound for the rate of depletion of A_1 due to the speciation reaction, then the material balances for species A_1 are

$$V\frac{dC_{A_1}}{dt} = -m\frac{d\bar{C}_{A_1}}{dt} - Vk^{*}C_{A_1} \tag{4}$$

with

$$C_{A_1}(0) = C^{0}_{A_1} \tag{5}$$

and

$$\frac{d\bar{C}_{A_1}}{dt} = \rho hs\left(\Gamma_{A_1}C_{A_1} - \bar{C}_{A_1}\right) \tag{6}$$

with

$$\bar{C}_{A_1}(0) = 0 \tag{7}$$

where m = mass of solid

V = volume of solution.

The material balances for species A_2 are

$$V\frac{dC_{A_2}}{dt} = -m\frac{d\bar{C}_{A_2}}{dt} + Vak^{*}C_{A_1} \tag{8}$$

with

$$C_{A_2}(0) = 0 \tag{9}$$

and

$$\frac{d\bar{C}_{A_2}}{dt} = \rho hs\left(\Gamma_{A_2} C_{A_2} - \bar{C}_{A_2}\right) \tag{10}$$

with

$$\bar{C}_{A_2}(0) = 0 \quad . \tag{11}$$

The solutions to Equations (4) and (6) with initial conditions given by Equations (5) and (7) can be obtained using Laplace transforms (see Addendum) and are

$$\frac{C_{A_1}}{C^0_{A_1}} = \frac{(b_1+\rho hs)}{\sqrt{b^2-4d}}\, e^{b_1 t} - \frac{(b_2+\rho hs)}{\sqrt{b^2-4d}}\, e^{b_2 t} \tag{12}$$

and

$$\bar{C}_{A_1} = \frac{C^0_A \rho hs \Gamma_{A_1}}{\sqrt{b^2-4d}} \left(e^{b_1 t} - e^{b_2 t}\right) \tag{13}$$

where $b = \rho hs\left(1 + \frac{m\Gamma_{A_1}}{V}\right) + k^*$

$$b_1 = -\frac{b + \sqrt{b^2-4d}}{2}$$

$$b_2 = -\frac{b - \sqrt{b^2-4d}}{2}$$

$$d = \rho h s k^* .$$

Again, for purposes of illustration, let the sorption equilibrium distribution function Γ_{A_2} for species $A_2 = 0$, and let the stoichiometric coefficient $a = 1$. Then the material balances for species A_2 are

$$\frac{dC_{A_2}}{dt} = k^* C_{A_1} \tag{14}$$

with

$$C_{A_2}(0) = 0$$

and

$$\overline{C}_{A_2} = 0 \quad .$$

The solution to Equation (14) with initial condition given by Equation (9) is (see Addendum)

$$C_{A_2} = \frac{k^* C^0_{A_1}}{\sqrt{b^2 - 4d}} \left[\left(\frac{b_1 + \rho hs}{b_1} \right) e^{b_1 t} - \left(\frac{b_2 + \rho hs}{b_2} \right) e^{b_2 t} - \rho hs \left(\frac{1}{b_1} - \frac{1}{b_2} \right) \right] \quad . \tag{15}$$

Batch Sorption Experiments

Generally, in batch sorption experiments a known volume V of a solution containing the nuclide of interest is contacted with a known mass m of solid. The initial radioactivity A_0 of the nuclide per unit volume of solution is known. The subsequent radioactivity A of the solution is monitored as a function of time, and when A appears to remain constant, the system is assumed to be at equilibrium. The amount of the nuclide sorbed by the solid is then calculated from V, values of A/A_0, and the respective sample volumes. For the case where $C_{A_2}(0) = 0$, $\Gamma_{A_2} = 0$, and the stoichiometric coefficient $a = 1$,

$$\frac{A}{A_0} = \frac{C_{A_1} + C_{A_2}}{C^0_{A_1}} \tag{16}$$

and from Equations (12) and (15),

$$\frac{A}{A_0} = \frac{C_{A_1} + C_{A_2}}{C^0_{A_1}} = 1 - Be^{-b_1 t}\left(1-e^{-\sqrt{b^2-4d}\ t}\right) \tag{17}$$

where $$B = \frac{m\Gamma_{A_1}}{V\sqrt{\left[1+\frac{M\Gamma_{A_1}}{V}+\frac{k^*}{\rho hs}\right]^2-\frac{4k^*}{\rho hs}}} .$$

As an example, consider a case in which Γ_{A_1} : a constant = 300 cm^3/gm. Assume that results from geochemical sensitivity analyses indicate that if a chemical speciation reaction occurs, the value of k^* must be less than 2/3 yr^{-1} (0.0018 day^{-1}) if cumulative radionuclide discharges are to comply with the EPA standard. In typical laboratory batch experiments, reasonable values for m, V, and ρha would be 1 gm, 100 cm^3, and 0.17 day^{-1} (sorption reaction half-life of about 1 day), respectively. If Γ_{A_1} and k^* are taken as 300 cm^3/gm and 0.0018 day^{-1}, respectively, then Equation (17) becomes

$$\frac{A}{A_0} = 1 - 0.75e^{-0.0005t}\left(1-e^{-0.68t}\right) . \tag{18}$$

Values of A/A_0 versus t for a hypothetical experiment described by Equation (18) are given on Figure 1 for $2 \leq t \leq 40$ days, and on Figure 2 for $1 \leq t \leq 2000$ days. From Figure 1, it can be seen that unless the precision in experimentally determined values of A/A_0 were very high, the experiment would appear to reach equilibrium during the interval between about 8 and 40 days. To detect the effects of the chemical speciation reaction, data for a much longer time interval would be required, as indicated on Figure 2. The time interval required to detect effects would depend on the precision in the experimental data.

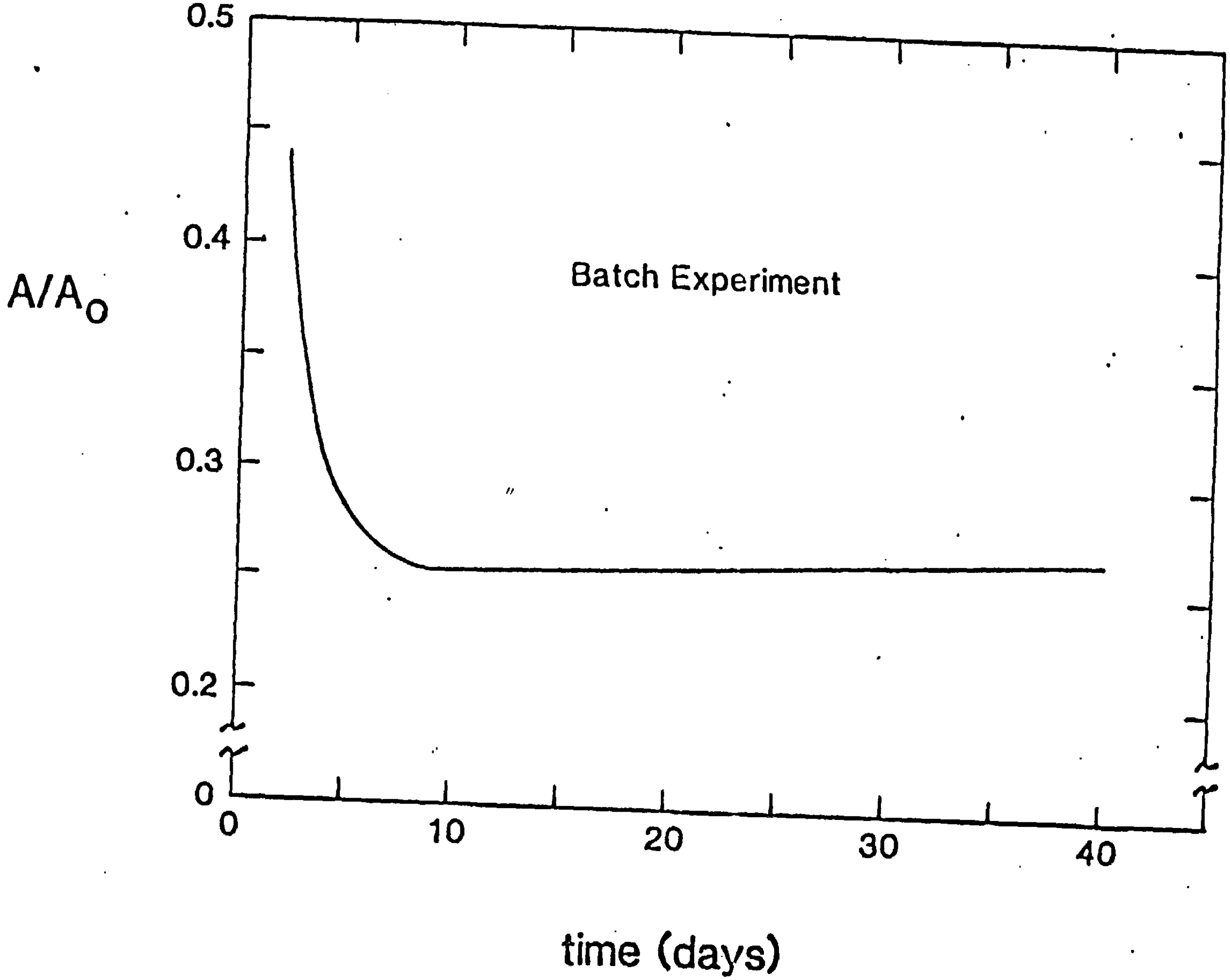

Figure 1. Values of A/A_0 Versus Time t for a Hypothetical Batch Sorption Experiment ($m = 1$ gm, $V = 100$ cm^3, $\Gamma_{A1} = 300$ cm^3/gm, $\rho hs = 0.17$ day^{-1}, $k^* = 0.0018$ day^{-1})

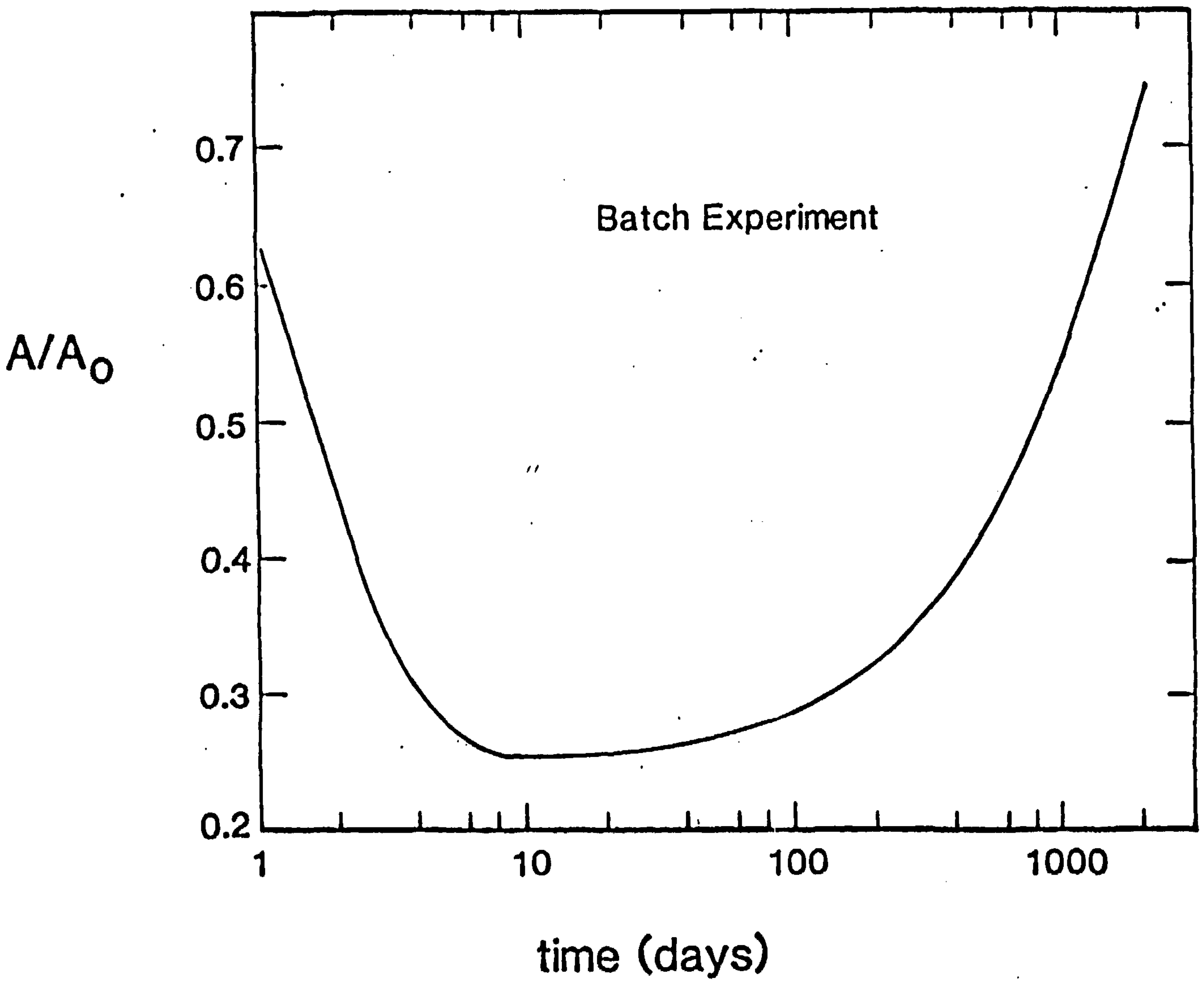

Figure 2. Values of A/A_0 Versus Time t for a Hypothetical Batch Sorption Experiment ($m = 1$ gm, $V = 100$ cm^3, $\Gamma_{A1} = 300$ cm^3/gm, $\rho hs = 0.17$ day^{-1}, $k^* = 0.0018$ day^{-1})

In general, sensitivity analyses can identify the combinations of values of Γ and k^* which could result in cumulative radionuclide discharges which violate the EPA standard. Knowing those values and the expected precision in experimental data, analyses similar to the above example could be used to define criteria for:

1. Designing batch sorption experiments which will be of sufficient duration to detect the effects of any chemical speciation reactions which might result in violations of the EPA standard; and
2. Evaluating data from previous experiments to determine if the effects of speciation reactions which could cause violation of the EPA standard would have been detected.

Conclusions

Batch sorption experiments should be examined closely to determine if chemical speciation reactions which may significantly affect cumulative radionuclide discharges could be detected. Criteria for evaluating data and designing experiments can be developed using analyses similar to those discussed above.

Addendum

Let $\tilde{C}_{A_1}(p)$ denote the Laplace transform of $C_{A_1}(t)$ with respect to t, and similarly define $\tilde{\bar{C}}_{A_1}(p)$. Then from Equations (4) through (7)

$$\tilde{C}_{A_1} = \frac{C_A^0(p+\rho hs)}{p^2 + \left[\rho hs(1+m\Gamma_{A_1}/V)+k^*\right]p + \rho hsk^*}$$

or

$$\tilde{C}_{A_1} = \frac{C_A^0(p+\rho hs)}{(p-b_1)(p-b_2)}$$

where b_1 and b_2 are defined above. Also,

$$\bar{\bar{C}}_{A_1} = \frac{\rho hs\Gamma_{A_1}\tilde{\bar{C}}_{A_1}}{p + \rho hs} \quad .$$

Using the residue theorem (see J. Crank, <u>The Mathematics of Diffusion</u>, Claredon Press, Oxford, 1975, pp. 26-27),

$$C_{A_1} = \frac{C^0_{A_1}}{\sqrt{b^2-4d}}\left[(b_1+\rho hs)e^{b_1 t} - (b_2+\rho hs)e^{b_2 t}\right] \tag{12}$$

and

$$\bar{C}_{A1} = \frac{C^0_{A_1}\rho hs\Gamma_{A_1}}{\sqrt{b^2-4d}}\left[e^{b_1 t}-e^{b_2 t}\right]$$

where b and d are defined above. Now, from Equation (14),

$$C_{A_2} = k^*\int_0^t C_{A_1}dt$$

or

$$C_{A_2} = \frac{k^*C^0_{A_1}}{\sqrt{b^2-4d}}\left[\left(\frac{b_1+\rho hs}{b_1}\right)e^{b_1 t} - \left(\frac{b_2+\rho hs}{b_2}\right)e^{b_2 t} - \rho hs\left(\frac{1}{b_1}-\frac{1}{b_2}\right)\right] \quad . \tag{15}$$

Then from Equations (12), (15), and (16)

$$\frac{A}{A_0} = \frac{C_{A_1} + C_{A_2}}{C^0_{A_1}} = 1 - Be^{-b_1 t}\left(1-e^{-\sqrt{b^2-4d}\ t}\right) \tag{17}$$

where B is defined above.