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DURABILITY EVALUATION OF RADIOACTIVE WASTE PRODUCTS

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I. IMPORTANCE OF DURABILITY EVALUATION OF RADIOACTIVE WASTE PRODUCT FORMS

A. Conversion of nuclear "wastes" to a durable, solid, essentially insoluble product will effectively limit transport of radionuclides during time required for decay processes.

B. Response to recent public concern regarding safety of perpetual nuclear waste storage requires delineation of dependably safe systems including waste product forms and interaction with storage environments.

II. DURABILITY EVALUATION PROCEDURES

A. Water contact with wastes is a possibility that must be considered during long-term storage.

B. Waste forms are subject to water attack and dissolution.

C. Therefore wastes are tested in the laboratory by leaching procedures to determine durability.

III. DISCUSS SUMMARY SUBMITTED TO AMERICAN NUCLEAR SOCIETY (ARH-SA-165-A)

A. Leaching equations (Figure 1).

1. $f = at^{1/2}$ describes fraction leached by a diffusion process. $t^{1/2}$ is characteristic of ideal diffusion. (Equation 1)

2. $f = at^{1/2} + bt$ fits some data better because of inclusion of bt to describe chemical attack. (Equation 2)

3. $f = kt^n$ used to describe approximately data that is better fitted by $f = at^{1/2} + bt$. (Equation 3)

4. $$f = \frac{C_0 F}{C_0 V}\left(\frac{4D}{\pi}\right)^{1/2} t^{1/2}$$

   where... Slide #27

   This equation shows the constants included in k, and can be arrived at by theoretical derivation. Note that C_0 and D are considered to be constants. (Equation 4)

B. Illustration of equations in ANS Summary Figure (Figure 2).

1. Log-log plot used since leaching equations yield straight lines with a slope equal to the value of the exponent of time. Also retains sensitivity at short times.

2. BIKO equation plots as curved line, leveling off at a value given by z and curvature determined by k.

3. BIKO equation fits early data better than straight line functions.

DISCLAIMER

C. Derivation of BIKO equation from conventional leaching equations (Figure 3).

1. A correction is made for changing concentrations in the leaching process. C_0 is eliminated in converting the leaching equation to terms of fraction leached. (Equation 5)

   a. Z is considered to be the fraction of a component subject to leaching as described by the leaching equation. Each Z may describe a different diffusion path.

   b. f is the fraction of the component that is leached. f is subtracted from correction factor Z so that the fraction leached does not exceed one and accounts for the component removed from the leached sample.

   c. The BIKO correction (Z-f) allows for a situation including more than one diffusion path and a finite amount of diffusible material.

2. Constants $\frac{C_0 F}{C_0 V}\left(\frac{4D}{\pi}\right)^{1/2}$ are consolidated as k. (Equation 6)

3. Quantities are multiplied; fraction f term is transposed. (Equation 7)

4. Solution for f gives the BIKO equation form. (Equation 8)

5. By fitting BIKO equations to experimental data, the exponent on time has been found to have three values: 1/2, 1 and 3/2. (Figure 4).

   a. 1/2 and 1 are taken from conventional leaching relationships as representing diffusion and chemical attack. (Equations 9 and 10)

   b. Exponent on time of 3/2 has been found to describe terminal leaching processes, i.e., when the fraction leached approaches one. (Equation 11)

   c. One, two or three of the BIKO equations may be required to describe leaching data. (Equation 12)

D. Current usage of BIKO equations.

1. The three terms of the equation fitted to the data shown in the ANS Summary (Figure 2) have been reduced to two terms that fit the data equally well or better (Figure 5).

2. The BIKO equations show the function of time involved, thereby indicating the leaching process involved.

3. The BIKO equations predict a leveling off effect, precluding the fraction leached greater than one predicted by conventional leaching equations.

IV. SEVERAL EXAMPLES OF BIKO FIT TO DATA

A. Atlantic Richfield Hanford Company data by M. J. Kupfer

1. Sodium data fitted by diffusion BIKO (Figure 6).

2. Silicon data fitted by corrosion BIKO (Figure 7).

3. Cesium data fitted by diffusion plus corrosion BIKO (Figure 8).

4. Strontium data fitted by diffusion plus corrosion BIKO (Figure 9).

B. Terminal leaching data

1. Terminal leaching and diffusion BIKO fitted to sodium data for devitrified glass of Hahn-Meitner-Institut (HMI) (complete removal of less durable phase) (Figure 10).

2. Terminal leaching of potassium from binary potassium silicate glass of Douglas and El-Shamy (Complete removal of less durable phase.) (Figure 11).

C. Processes other than leaching

1. BIKO equations have been fitted to ion-exchange data.

2. BIKO equations have been fitted to xenon diffusion from UO_2 fuel elements.

V. HYPOTHETICAL COMPLETE LEACHING PROCESS (Figure 12)

A. k values used for BIKO ($t^{1/2}$) and BIKO (t) have been found to fit actual leaching data.

B. k value used for BIKO ($t^{3/2}$) has not been observed since leach data does not extend to long time required.

1. Non-durable products have exhibited the terminal leaching process, but at short times.

2. Durable products are expected to exhibit a similar process, but at long times.

VI. FEATURES OF BIKO EQUATIONS (Figure 13)

A. Provides a correction for changing concentration with time; the form of the correction may allow for changes of concentration in the leached sample or leaching solution.

B. Approaches one as the fraction leached for infinite leaching times.

C. Sum of BIKO equations describes concurrent leaching processes.

D. Provides a set of numbers that characterize the leaching data.

E. Fits all the data examined to date.

VII. APPLICATION OF BIKO CONSTANTS TO DURABILITY EVALUATION

A. Constant k (Figure 14).

1. High value of k means that the component described by that k is leached from the sample in a short time.

2. Low value of k produces the leveling off effect at long times; indicates high durability.

3. Values of k that have been observed to date for each BIKO term are shown; range of observed k is different for each BIKO term.

4. k is noted to be a reciprocal time constant; further investigation is underway.

B. Fraction Z.

1. Z is defined as the fraction of a component subject to removal from the leached sample according to the BIKO term describing its removal.

2. A durable product has a low Z value.

C. Exponent of time.

1. $t^{1/2}$ diffusion process exhibits a rate that decreases with time which is a desirable durability characteristic.

2. Linear time process exhibits a rate that is constant with time, indicating a less durable product.

3. $t^{3/2}$ terminal process indicates a rate that increases with time, an undesirable property.

VIII. CONCLUSION

A. Simplicity of BIKO terms facilitates fitting of leaching data.

B. Constants obtained from fitted BIKO terms indicate durability qualities.

C. Evaluation and comparison of BIKO constants aid in interpreting leaching data and provide insights concerning leaching processes.

D. BIKO equation form may describe other ion-exchange and diffusion processes.

IX. REFERENCES

(1) Saidl, J. and J. Ralkova, "Immobilization of Strontium and Cesium by Fixation of Radioactive Waste in Basalt," Collection, Czechoslov. Commun., 31, 871, (1966).

(2) Kupfer, J. J., Personal Communication, ARHCO (Unpublished), (1970).

(3) Heimerl, W., H. Heine, L. Kahl, H. W. Levi, W. Lutze, G. Malow, E. Schiewer and P. Schuber, Research on Glasses for Fission Product Fixation, Hahn-Meitner-Institut Berline G m.b.H., Report No. HMI-B-109, September, (1971).

(4) Douglas, R. W., and T. M. M. El-Shamy, "Reactions of Glass with Aqueous Solutions," J. Amer. Ceramic Soc., 50, No. 1, (1967).

$$f = at^{1/2} \tag{1}$$

$$f = at^{1/2} + bt \tag{2}$$

$$f = kt^{n} \tag{3}$$

$$f = \left(\frac{F}{V}\right)\left(\frac{4\,Dt}{\pi}\right)^{1/2} \tag{4}$$

FIGURE 1. CONVENTIONAL LEACHING EQUATIONS

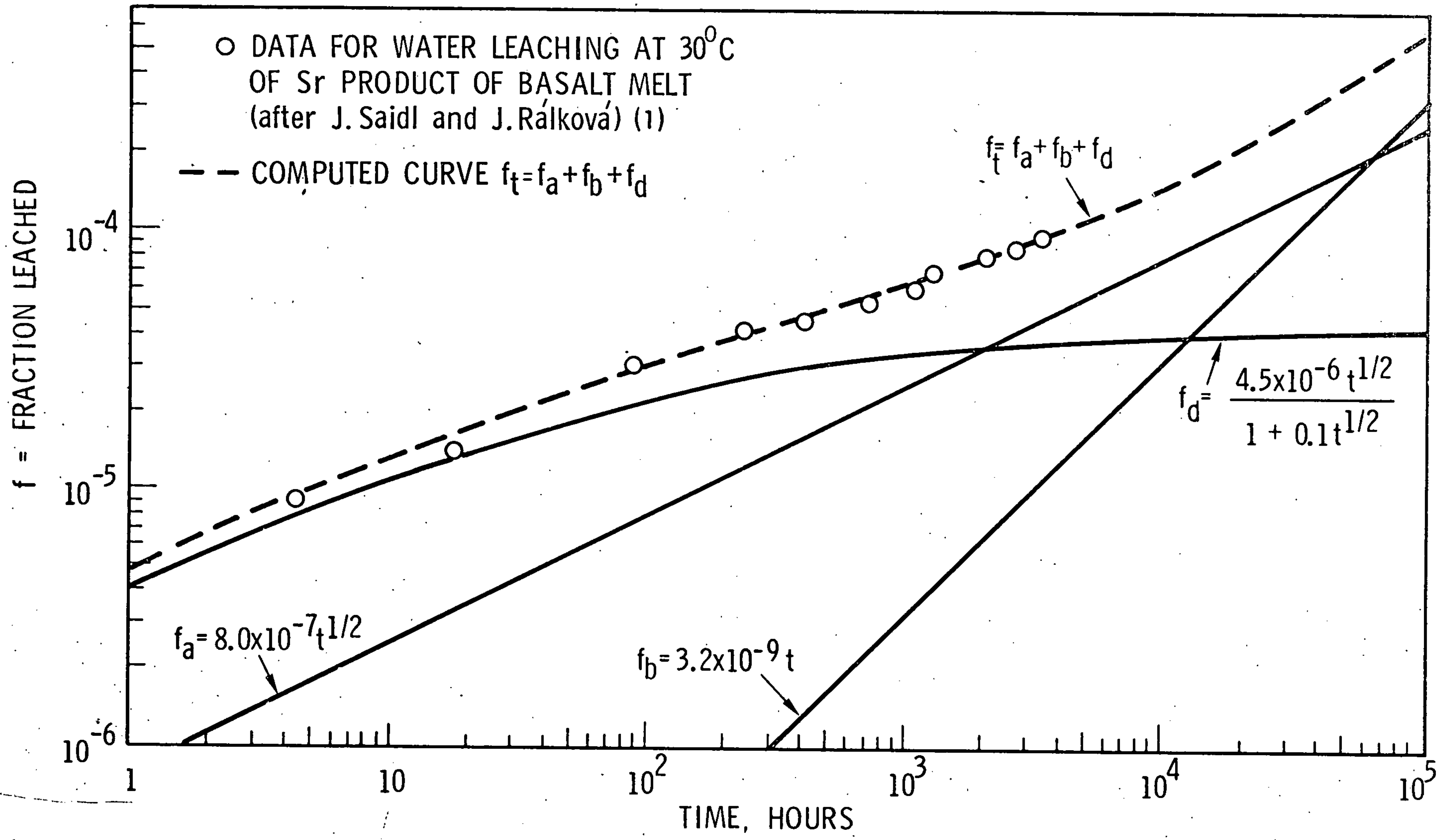

FIGURE 2. Sr^{++} LEACH DATA FOR BASALT AT 30°C

BIKO DERIVATION

$$f = (z-f)\left(\frac{F}{V}\right)\left(\frac{4Dt}{\pi}\right)^{1/2} \qquad (5)$$

$$f = (z-f)\,kt^{1/2} \qquad (6)$$

$$f + fkt^{1/2} = zkt^{1/2} \qquad (7)$$

$$f = \frac{zkt^{1/2}}{1 + kt^{1/2}} \qquad (8)$$

FIGURE 3. DERIVATION OF BIKO EQUATION FROM A CONVENTIONAL LEACHING EQUATION

BIKO EQUATIONS

$$f_d = \frac{zkt^{1/2}}{1 + kt^{1/2}}$$

$$f_c = \frac{zkt}{1 + kt}$$

$$f_e = \frac{zkt^{3/2}}{1 + kt^{3/2}}$$

$$f_t = f_d + f_c + f_e$$

FIGURE 4. THE FORM OF THE BIKO EQUATIONS

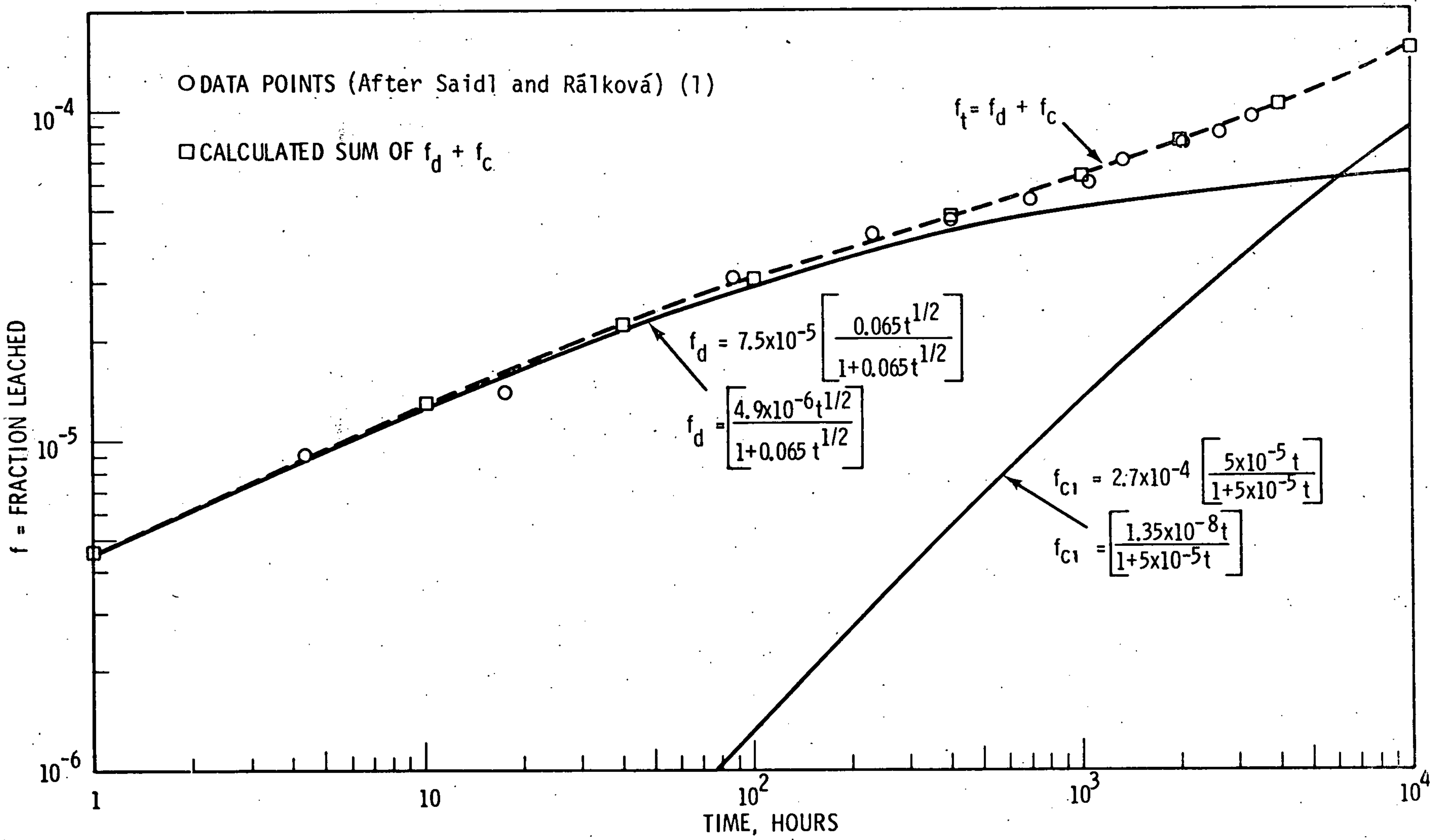

FIGURE 5. COMPARISON OF SUM OF TWO BIKO RELATIONSHIPS TO DATA FOR LEACHING OF STRONTIUM FROM BASALT AT 30°C

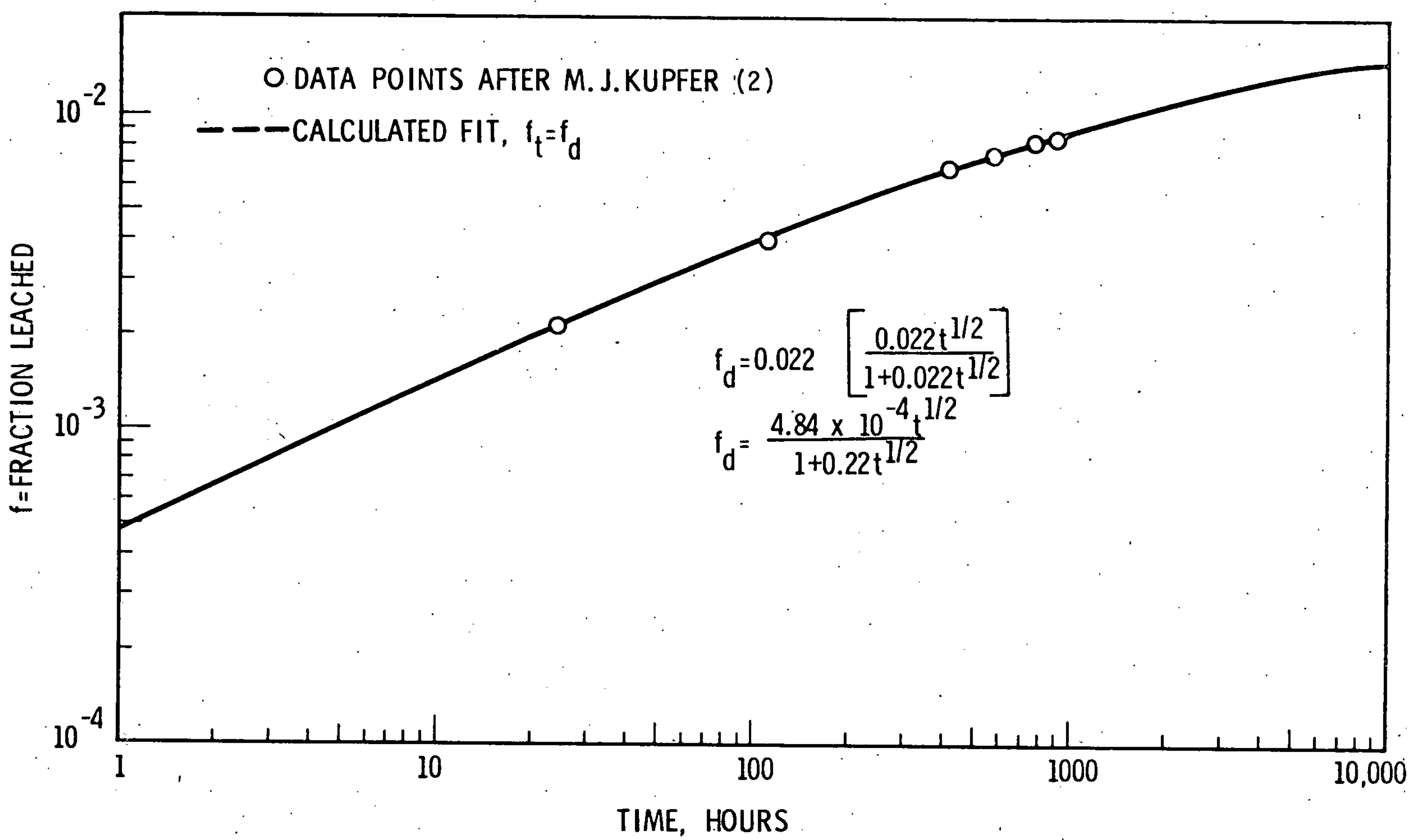

FIGURE 6. COMPARISON OF BIKO RELATIONSHIPS TO DATA OF M.J. KUPFER FOR LEACHING OF Na FROM #B OPTIMUM FORMULATION

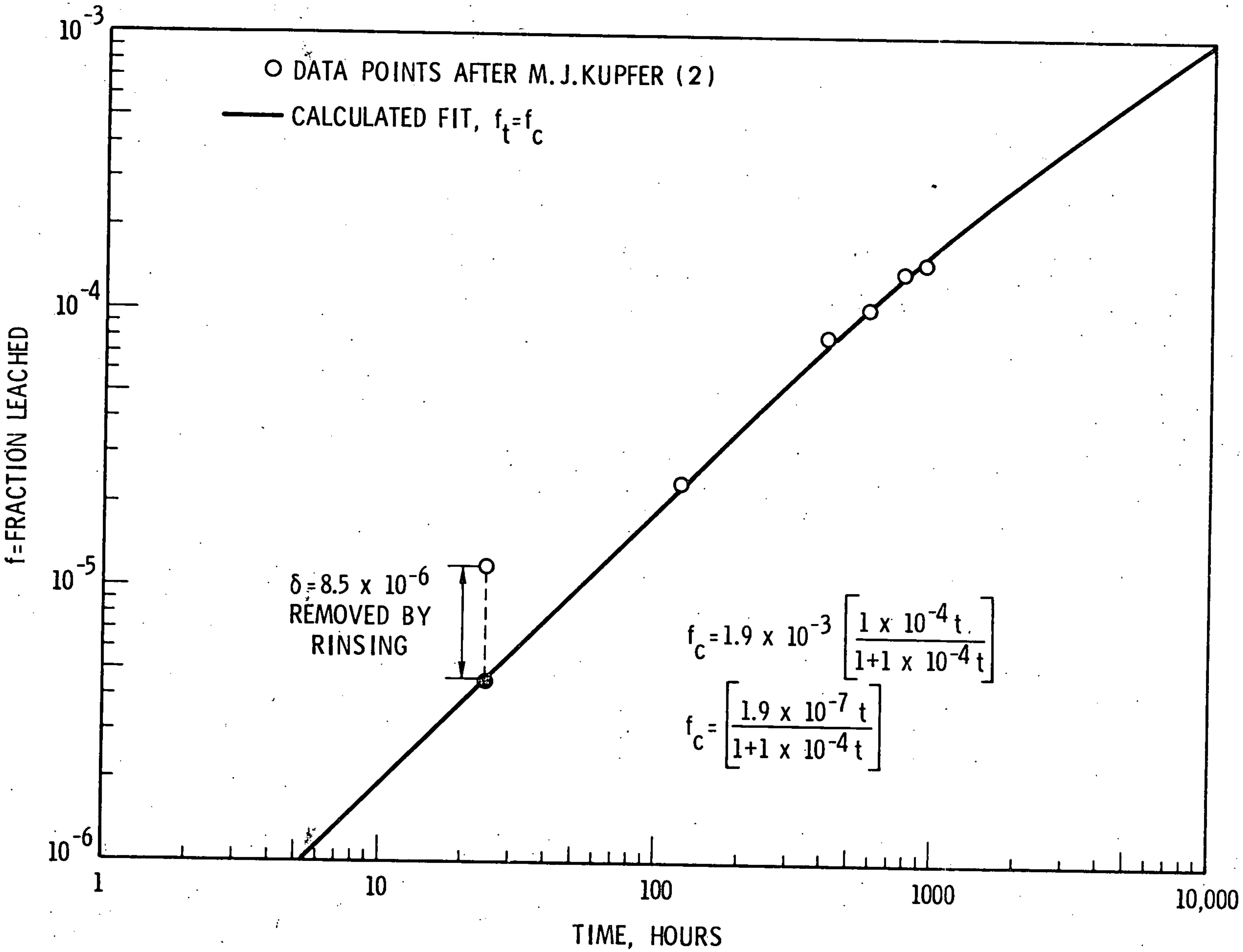

FIGURE 7. COMPARISON OF BIKO RELATIONSHIPS TO DATA OF M. J. KUPFER FOR LEACHING OF Si FROM #B OPTIMUM FORMULATION

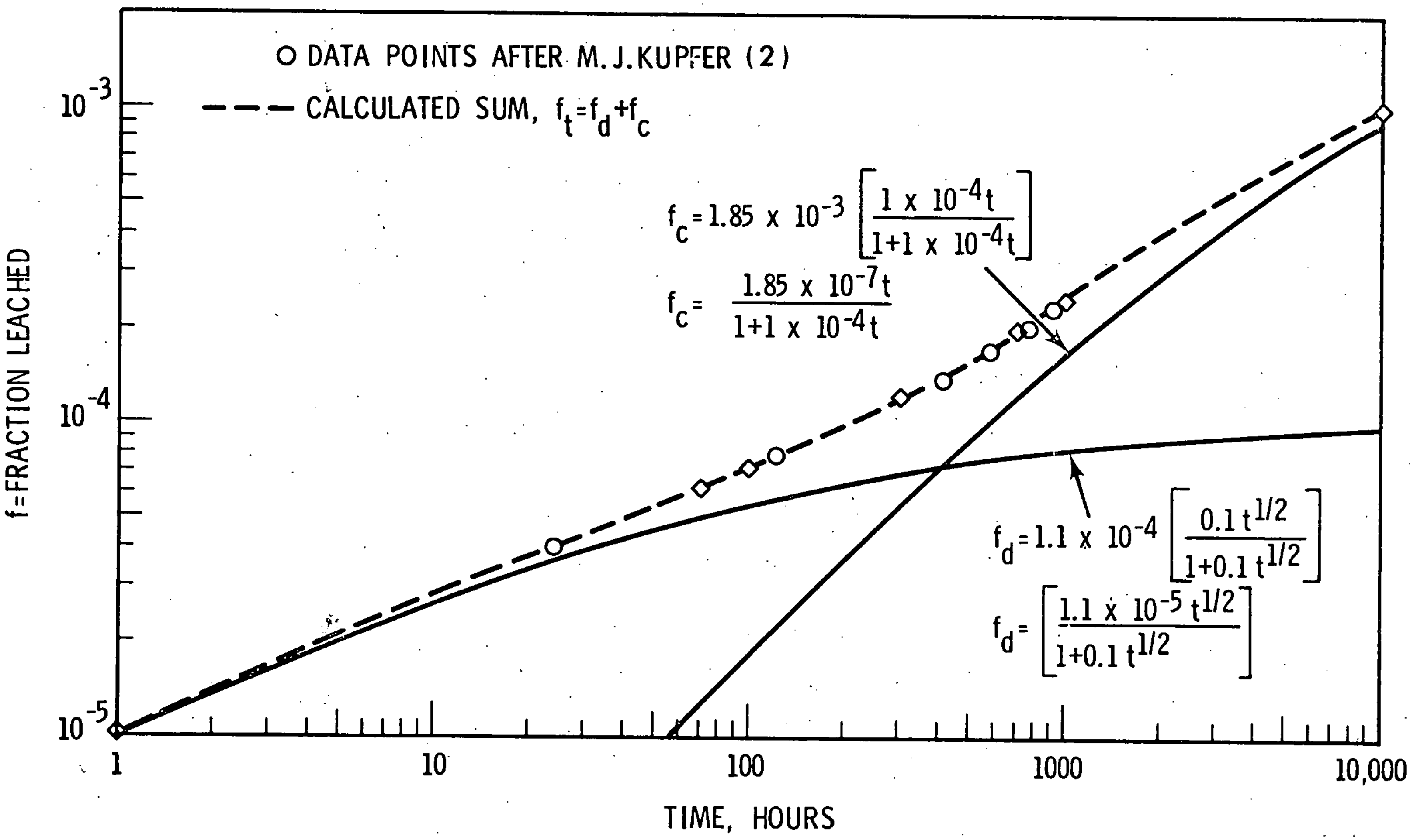

FIGURE 8. COMPARISON OF BIKO RELATIONSHIPS TO DATA OF M. J. KUPFER FOR LEACHING OF Cs FROM #B OPTIMUM FORMULATION

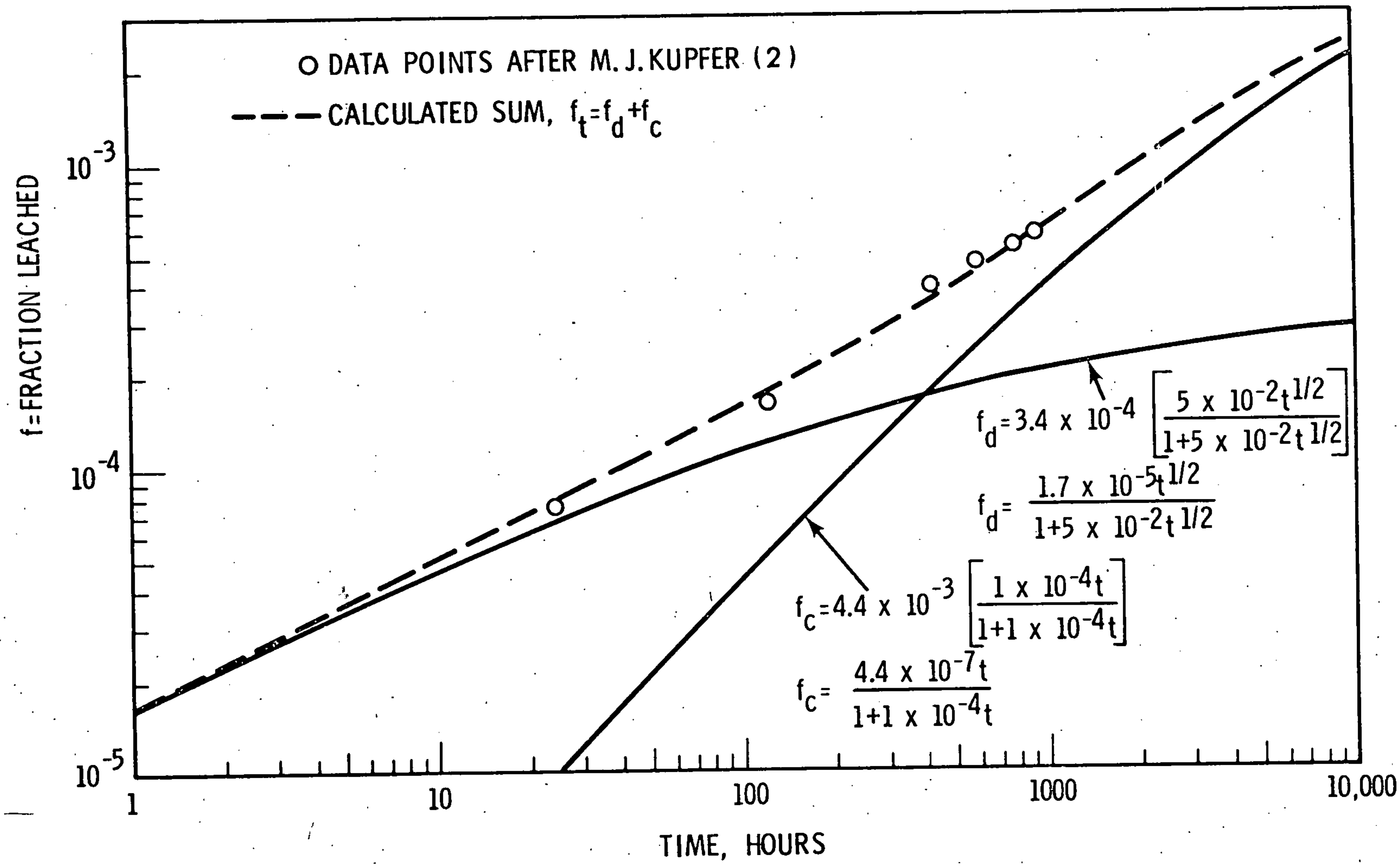

FIGURE 9. COMPARISON OF BIKO RELATIONSHIPS TO DATA OF M.J. KUPFER FOR LEACHING OF Sr FROM #B OPTIMUM FORMUALTION

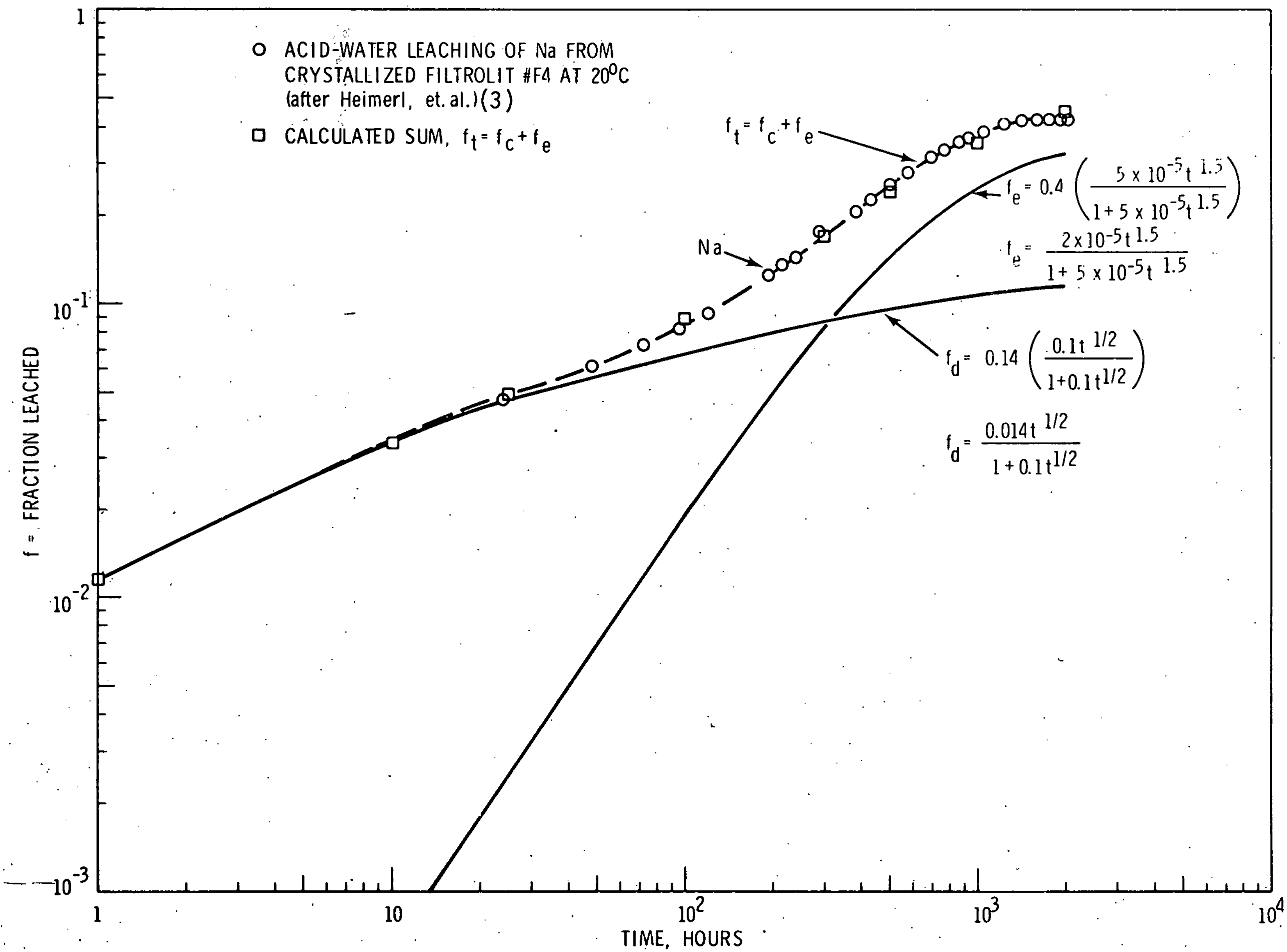

FIGURE 10. COMPARISON OF BIKO RELATIONSHIPS WITH DATA FOR LEACHING OF SODIUM FROM CRYSTALLIZED FILTROLIT #F4

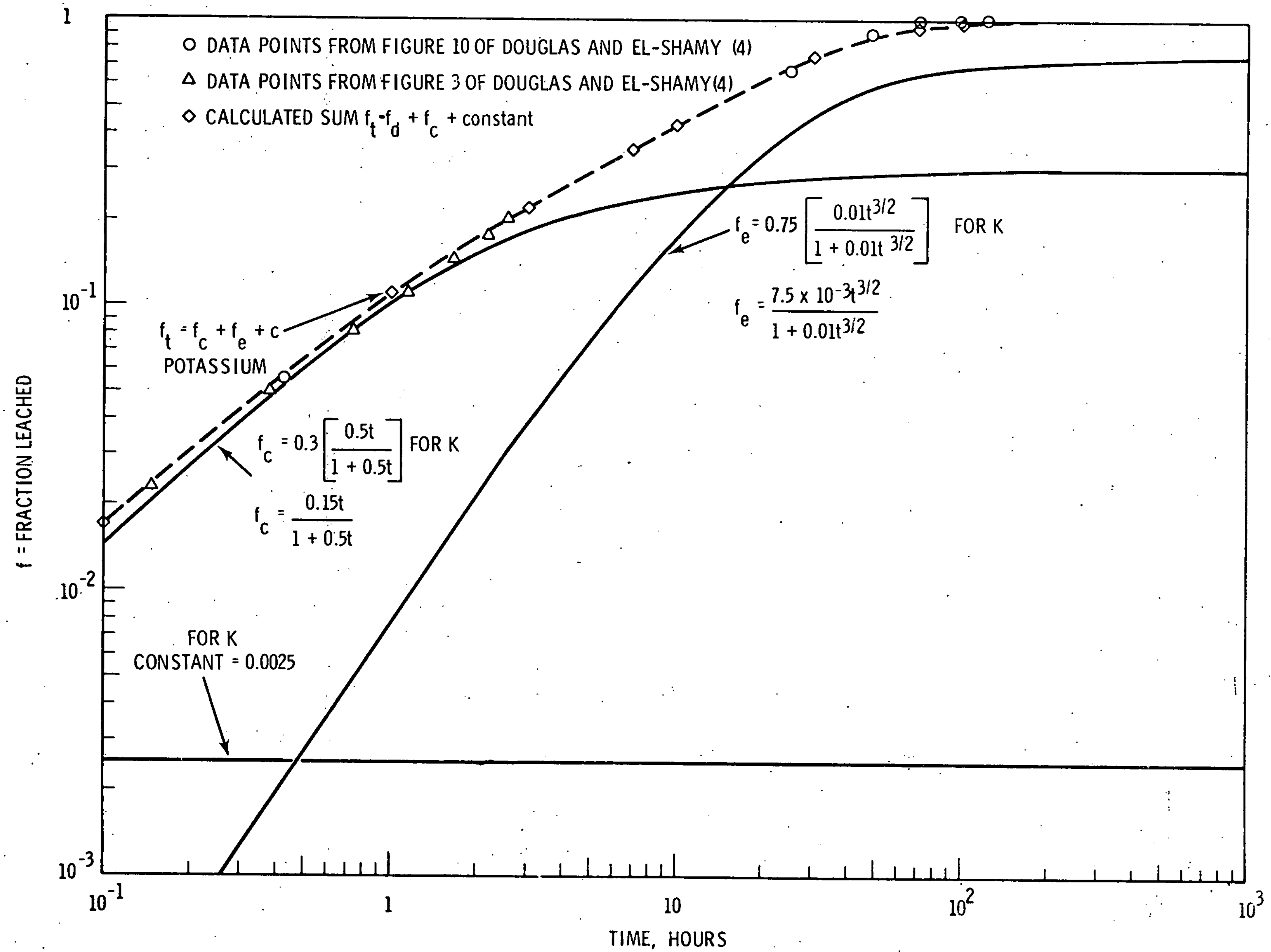

FIGURE 11. BIKO CURVES FOR THE 100 PERCENT LEACHING OF POTASSIUM FROM A $15K_2O \cdot 85SiO_2$ GLASS

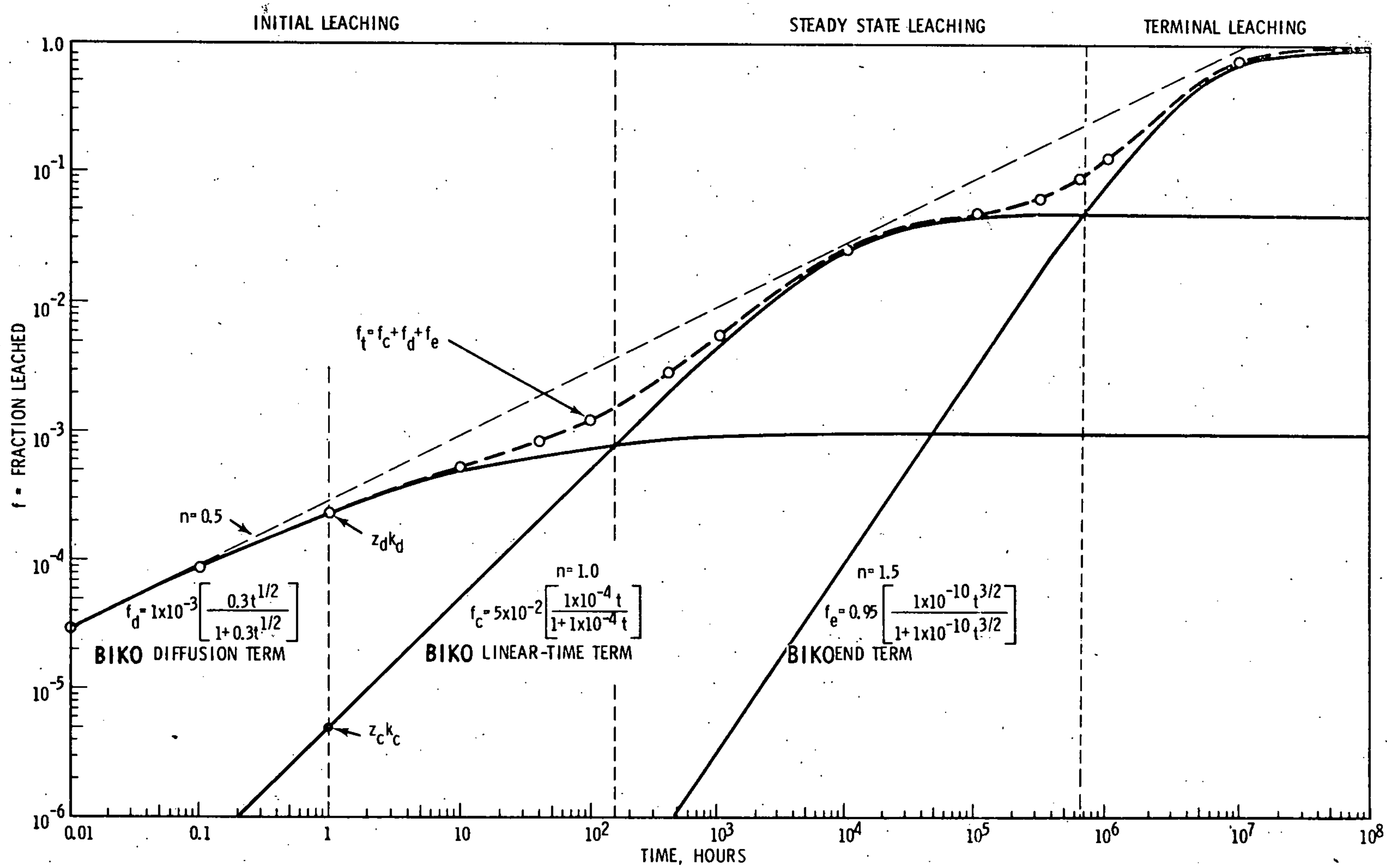

FIGURE 12. GRAPHICAL DEMONSTRATION OF THREE BIKO EQUATIONS AND THREE TIME PERIODS DURING LEACHING

FEATURES OF BIKO EQUATIONS

1. CORRECTS FOR CONCENTRATION
2. APPROACHES FINITE FRACTION
3. DESCRIBES CONCURRENT PROCESSES
4. YIELDS CHARACTERISTIC CONSTANTS
5. FITS ALL DATA STUDIED

FIGURE 13. USEFUL FEATURES OF THE BIKO EQUATIONS

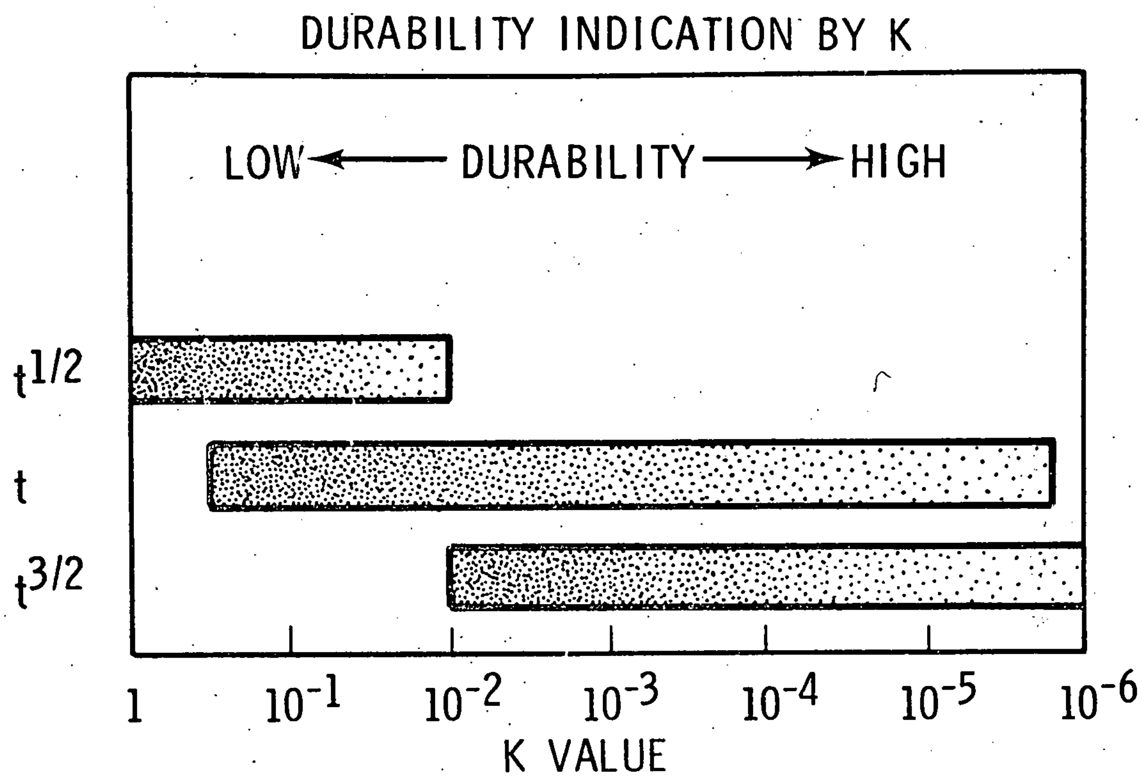

FIGURE 14. INDICATION OF DURABILITY BY THE BIKO CONSTANT K