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PROGRESSIVE ACID DISSOLUTION AS A TECHNIQUE
FOR DETERMINING THE POTASSIUM SUPPLY
OF FOREST SOILS

By

Christopher W. Bowen

B.A., Carleton College, 1970

Presented in partial fulfillment of the requirements for the degree of

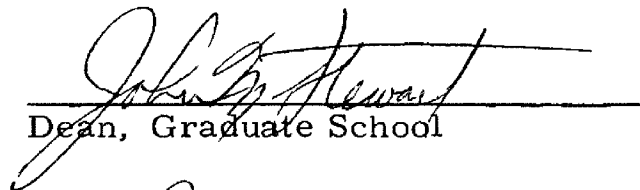
Master of Science

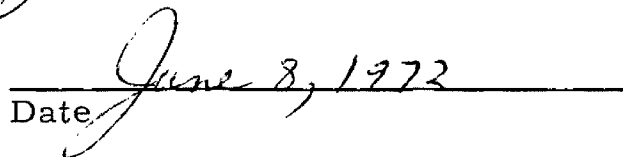
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CHAPTER I

INTRODUCTION

An important type of ecological investigation and one which is becoming more common is the analysis of nutrient cycling within forest ecosystems (Borman and Likens, 1967) (Cole and Gessel, 1968). Such studies are essential to understanding the basis of biological productivity, to developing sound plans for resource management, and to maintaining environmental quality.

Studies of nutrient cycling within ecosystems have consisted of analysis of the nutrient contents of the major biotic and abiotic components of the ecosystem, the rates of transfer between these components, and the additions to and losses of nutrients from the ecosystem. For components such as the dominant trees, such analyses consist of determination of the total nutrient content of the tree, partitioning of these nutrients between the various structural and functional subunits of the tree, and rates of uptake and return of these nutrients from and to their storage compartments within the ecosystem. For a nutrient such as potassium this last type of analysis means determination of the annual rate of uptake and return of potassium to the soil reservoir through such mechanisms as plant absorption, litter fall, and leaching from leaves and stems by rainfall.

While detailed analysis as described above has been carried out on the major biotic components of forest ecosystems, the forest soil has in the past generally been treated only as a rather uniform compartment whose major function is to supply nutrients for plant growth. Workers at the University of Washington have investigated topics related to the movement of nutrient ions through the soil (McColl, 1969) (McColl and Cole, 1968) (Grier and Cole, 1971) (Gessel and Cole, 1965) (Cole and Ballard, 1970) (Cole and Gessel, 1963). However, work on the specific sites of potassium storage within forest soils is limited.

It is generally believed (Reitemeier, 1951) (Fried and Broeshart, 1967) (Hood, et al., 1956) that the supply of potassium in soils can be represented as an equilibrium between soluble, exchangeable, and nonexchangeable or fixed forms. Of these, exchangeable potassium represents that portion of the soil potassium which is directly and immediately available for plant absorption. Measurement of exchangeable potassium to represent a soil's potassium supplying power is one which is widely used in annual crop agriculture. The primary value of determinations of exchangeable potassium in agriculture is an index of fertilizer requirements (Schmitz and Pratt, 1953).

Measurement of the potassium exchangeable with extractants like ammonium acetate, hydrochloric acid, nitric acid, and others

has also been used in forestry research. However, like the agricultural studies, these studies were based on a need to determine whether fertilization was necessary and to show correlation between low values of exchangeable potassium and potassium deficiency in trees. Leaf (1968) provides an excellent summary of this work. Because exchangeable potassium is believed to represent that portion of a soil's potassium which is immediately available for uptake by plants, it is a valuable tool in assessing immediate nutrient requirements. However, this does not necessarily mean that measurements of exchangeable potassium provide a complete index of the soil potassium reservoir directly involved in nutrient cycling. It has, however, been used for this purpose.

For instance a study on the distribution and cycling of various nutrients in a second-growth Douglas fir (Pseudotsuga menzeisii) ecosystem by Cole, Gessel, and Dice (1967) considered the potassium exchangeable with pH 7, 1 normal ammonium acetate as providing an adequate measure of the soil's potassium reservoir. This method of determining the magnitude of the potassium reservoir available for plant growth may have some shortcomings when considering long-term as well as short-term cycling and is certainly inadequate to describe the complete situation with respect to soil potassium (Nelson, 1959) (Garmon, 1957).

It is hoped that the results of this investigation will provide a better estimate of the soil potassium reservoir involved in nutrient cycling than does exchangeable potassium. A better estimate would help account for the low value of twelve years calculated by Cole, Gessel, and Dice (1967) as the length of time the Cedar River ecosystem could continue growing at its present rate before exhausting its potassium supply.

A number of different experiments have demonstrated that when a soil's exchangeable potassium is removed, another reservoir of potassium in the soil is capable of replenishing the exchangeable compartment (Pratt, et al., 1956) (Reitemeier, 1951). The fact that exchangeable potassium is readily replenished indicates that a complete measurement of soil potassium cannot be obtained from measurements of exchangeable potassium alone, because rather than representing the total soil reservoir, exchangeable potassium is but one phase of a series of complex forms which are in dynamic equilibria. In studies of nutrient cycling, information about the total soil potassium reservoir, the proportions held in different forms, and the rates of exchange between these forms is necessary.

Data on total soil potassium alone is also insufficient for purposes of considering the cycling of potassium through an ecosystem. Total potassium data describes only the amount of potassium potentially available over geologic time and is insufficient to describe rates

of release to plants or weathering rate. Even a combination of total potassium with exchangeable potassium falls short of an adequate description of the soil system for the purposes of nutrient cycling studies.

In view of the inadequacies of present methods of determining soil potassium for nutrient cycling studies I decided to search for a method which could more completely describe the nature of the potassium reservoir of a forest soil. After several preliminary approaches had been tried, the technique which I selected was progressive acid dissolution. Progressive acid dissolution has been used by geologists to describe rather precisely the amount and distribution of potassium in some clays. I hoped to discover first whether progressive acid dissolution could be applied to soils, and if so, whether it could provide the kind of information needed to properly characterize the status of soil potassium for studies of nutrient cycling.

Progressive acid dissolution differentiates between cations bound by different energies to soil particles. The fraction of the total soil reservoir of the cations bound at each energy can also be determined. Thus, my objective in using this technique was to make a determination of the quantity of potassium within each soil storage compartment, to measure the bonding energies in each compartment, and to speculate upon the rates of release of potassium from each compartment.

The Everett Soil from the Allen E. Thompson Research Site in the Cedar River watershed near Seattle, Washington was used for the purpose of this investigation. This soil was selected because of the availability of data on potassium cycling at this site (collected as a part of the Coniferous Biome section of the International Biological Program's analysis of ecosystems) and of data on the morphology and mineralogy of this soil collected by Schlichte (1968). My investigation should complement past and ongoing research on nutrient cycling within the Douglas fir ecosystem at this site.

CHAPTER II

LITERATURE REVIEW

The Everett Soil used in this research was formed on the coarse gravelly outwash deposited by the Glacial Wilderness River. Gravel content was sixty-four per cent by dry weight. Drainage was excessive and silt and clay content was low. The Everett Soil Series belongs to the Brown Podzolic Great Soil Group and has been classified as a Typic Haplorthod, coarse loamy, over sandy, skeletal mixed, mesic soil according to the Seventh Approximation (Schlichte, 1968).

In general potassium in a soil can be viewed as being in an equilibrium between a number of different forms. The ultimate source of potassium in soils is from the weathering of primary minerals containing potassium. These primary minerals are chiefly the potassium feldspars which include orthoclase, microcline, adularia, and sandine (Jackson, 1964), and are most frequently found in the sand and silt fractions of the soil.

Schlichte (1968) found that the potassium containing feldspars range from 18.7 to 40 per cent of the light minerals in the fine sand fraction of the Everett Soil and also found a number of potassium-bearing heavy minerals.

Potassium is also found in the layer silicates of secondary minerals. Layer silicates form an important part of soil clays and are also commonly components of the larger size fractions. The basic crystal structure of the layer silicates consists of silicon tetrahedra (SiO_4^-) which share adjacent oxygens, and octahedra of an aluminum, iron, or magnesium ion surrounded by six oxygen or hydroxyl ions which are shared between adjacent octahedra. The silicon tetrahedra form a sheet as do the octahedra and the two types of sheets are joined by having each apical oxygen from the tetrahedral sheet replace a hydroxyl ion in the octahedral sheet (see Figure 1). By varying the ratio of tetrahedral to octahedral sheets (2 tetrahedral: 1 octahedral, 1 tetrahedral: 1 octahedral, or 2 tetrahedral: 2 octahedral) and by substitution of ions in the sheets, the various types of layer silicates are formed (Jackson, 1964). These different types of layer silicates are in turn responsible for many of the differences in chemical properties displayed by different soils.

Schlichte (1968) found chlorite, vermiculite, and kaolinite in the coarse clay fraction of the Everett Soil. But he noted that the medium plus fine clay fractions of all horizons consisted largely of amorphous material and that quartz and feldspar were relatively abundant in those same fractions.

When less positively charged ions are substituted for the more highly charged ions like Si^{+4} and Al^{+3} , the result is a crystal lattice

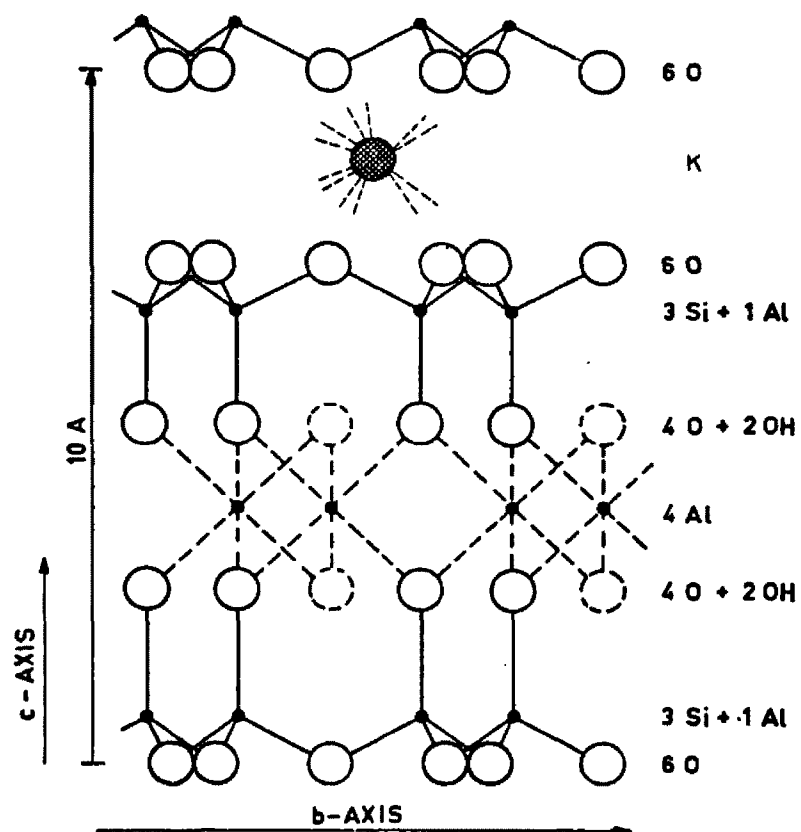


Fig. 1. --A Schematic Diagram of Muscovite,
a 2:1 Layer Silicate (Fried and
Broeshart, 1967)

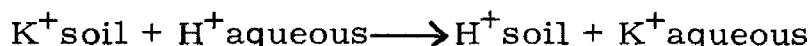
structure with a net negative charge. This negative charge is neutralized by adsorption of cations on the surface of the lattice structure and by the cations which are held between adjacent lattice structures. Cations bound on these two sites are important sources of the nutrients needed for plant growth.

The potassium ions held in interlayer positions, those held as adsorbed ions on the surface of particles, and those in the soil solution are thought to be in equilibrium with one another (Reitemeier, 1951). The potassium held in primary minerals and slowly released by weathering is also a part of this equilibrium. In addition to the ions held on the surfaces of mineral particles, ions are also held on the surfaces of particles of soil organic matter which also possesses exchange sites capable of adsorbing ions (Salomon and Smith, 1957).

Thus there are several specific sites such as primary minerals, interlayer positions in layer silicates, surfaces of mineral particles, and surfaces of soil organic matter particles at which potassium is held in soils. It is likely that each of these sites has a bonding energy different from all the others. If such is the case, progressive acid dissolution is a technique well suited to testing the hypothesis that potassium is held at a number of different sites, each with a specific energy, and each releasing potassium at a different rate.

In progressive acid dissolution the soil is placed in a dilute acid. The hydrogen ions in the solution replace the potassium and

other soil cations. For the monovalent cation K^+ the equation for the displacement reaction is:



For sufficiently concentrated acid solutions, the reaction would be essentially irreversible since the rate of the forward reaction would be many times greater than that of the reverse reaction. This follows from the Law of Mass Action which states that the rate of the forward reaction is proportional to the concentrations of the reactants (which are great in this case) while the rate of the reverse reaction is proportional to the concentrations of the products (which are very small in this case).

My primary concern in this experiment was to determine the rate or rates at which this reaction proceeds. Although this reaction was created artificially in the laboratory, it should be sufficiently similar to that occurring in nature to mimic under greatly accelerated rates the reaction which occurs naturally in forest soils. If the reaction is a first-order reaction, the rate of potassium removal will be proportional to the concentration of potassium in the soil. A plot of the natural logarithm of the per cent of potassium remaining versus time should give a straight line as shown in Figure 2 (Moore, 1962). The slope of this line is equivalent to the first-order rate constant.

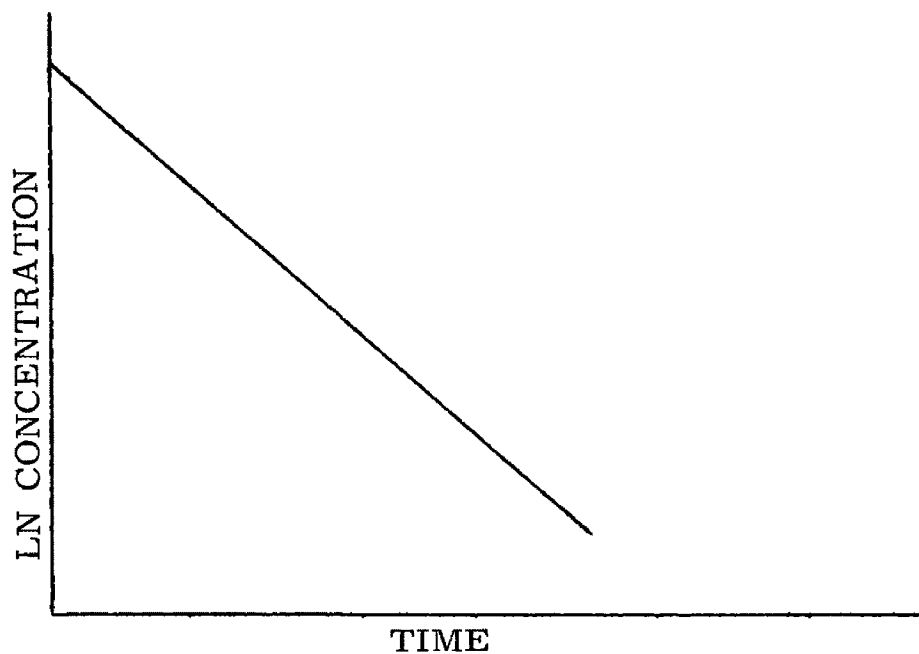


Fig. 2. --Ln Concentration vs. Time for a First-Order Reaction

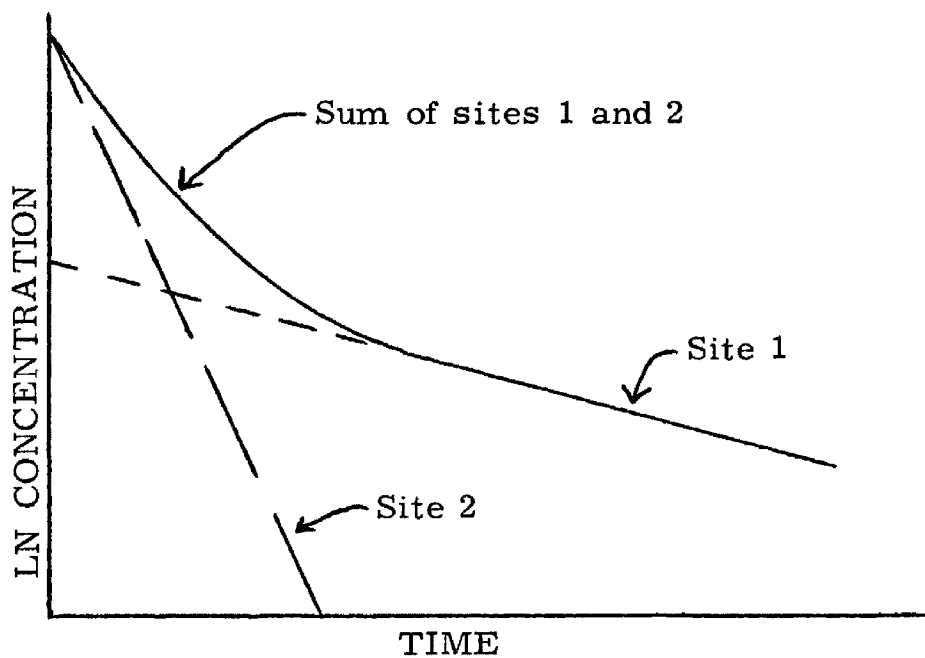


Fig. 3. --Ln Concentration vs. Time for an Ion Being Removed at Two Different Rates

If the potassium in the soil is bonded in two different sites and if the strength of the bonding at each site is different, then progressive acid dissolution will remove the potassium at two different rates. If both reactions are first-order, the graph of natural log of concentration remaining versus time will be a curve which is the sum of two straight lines and will appear as illustrated by Figure 3. When there are more than two discrete first-order reactions going on, the curve retains the general form illustrated by Figure 3.

Isolation of the effect of each independent rate on the total removal of potassium is made by deconvolving the curve. The curve is deconvolved by subtracting the contribution by the potassium removed at the lowest rate from the total curve followed by normalization of the remaining portion of total potassium to 100 per cent.

Thompson (1971) has found the removal of potassium from some clays to be a first-order reaction, and thus there was reason to expect that a similar relationship would be found in studying a soil.

CHAPTER III

METHODS

Progressive Acid Dissolution Technique

The method used in this investigation is a modification of the method used by Thompson (1971).

The soil used in this experiment was collected from the upper six inches of the soil profile, sieved through a two mm mesh, and air dried. A known quantity (about ten grams) of this soil was magnetically stirred in 250 ml of 0.5 normal HCl at a constant temperature. Temperature was maintained at a constant level by immersing beakers containing the sample and acid in a constant temperature water bath. After stirring for a known interval of time the sample was quickly removed from the constant temperature bath and centrifuged at high speed in order to separate the soil sample and extracting solution. The supernatant liquid was then pipetted off and a portion of it saved for analysis. Two hundred fifty ml of fresh, preheated acid was then added to the sample and this mixture was returned to the constant temperature bath and magnetic stirrer for additional extraction. This process was repeated many times up to a total time of about 230 hours.

Two hundred fifty ml of 0.5 normal HCl was used to maintain an excess of H^+ over K^+ and other ions, and to insure that the concentration of potassium ions in solution was sufficient to allow good quantitative determination. The samples of supernatant were stored in polyethylene bottles until analysis. Analysis for potassium was carried out on a Beckman DU-2 flame photometer at a wavelength of 768 $m\mu$ using an oxygen-hydrogen flame. The time between removal of the sample from the water bath and removal of the supernatant liquid from the sample was kept short in comparison to time spent in the water bath in order to reduce possible error.

Total Potassium Analysis

Samples of the air dried soil were separated by use of a sample splitter to insure homogeneity and then ground in a ball mill to reduce the size of large particles. The samples were weighed, placed in teflon beakers, and then digested according to the following procedure.

To a soil sample of two to three grams was added approximately 20 ml of water, 50 ml of hydrofluoric acid, and 25 ml of nitric acid. This mixture was allowed to stand for two hours to digest the organic matter. Ten milliliters of perchloric acid was added and the digestion was fumed on a hot plate while being magnetically stirred. Additional hydrofluoric acid was added as needed to complete the

digestion. The inside of the beaker was washed with water. Approximately 200 ml of concentrated hydrochloric acid was then added, and the solution was heated until all salts were dissolved. The solution was placed in a 250 ml volumetric flask, cooled, and brought to volume with distilled water. This solution was then diluted with water in order to facilitate analysis on the Beckman DU-2 flame photometer.

CHAPTER IV

RESULTS

The average of three determinations of total potassium content for the Everett Soil was a value of 0.826 per cent potassium by weight. Standard deviation of this mean was .0038.

After a number of preliminary runs, two progressive acid dissolutions were made at a temperature of 50°C. These two runs are referred to as runs (Samples) one and two. Table 1 shows the results of the progressive acid dissolutions of Samples one and two. Figures 4 and 7 are the total potassium dissolution curves derived by plotting the natural logarithm of the per cent of the total potassium remaining in the soil as a function of the length of extraction time.

The most significant feature of these total potassium removal curves is their general form. Since the results of the two dissolutions at 50°C are nearly identical I will discuss only Figures 4, 5, and 6 (representing Sample one) as representative of progressive acid dissolution at 50°C. The same discussion applies to the results from Sample two (Figures 7, 8, and 9).

Figure 4 shows an initial steep drop in the percentage of total potassium remaining. The natural log of per cent potassium remaining

decreases to a constant rate of removal at times greater than about forty hours. The portion of this curve which is linear within experimental error can be interpreted as representing a first-order reaction. The slope of this linear portion of the graph gives a first-order reaction rate constant (K_1) of 4.01×10^{-4} per hour. If the linear portion of the curve is extrapolated back to $t=0$ the intercept indicates that approximately ninety-six per cent of the total potassium is removed at the K_1 rate.

The non-linear portion of the curve at times less than about forty hours indicates a higher rate of removal which is the sum of the K_1 rate and one or more additional rates. Determination of this more rapid rate is made by deconvolution of the portion of the curve for less than forty hours. This results in the curve shown in Figure 5, which represents all potassium held less firmly than that removed at the lowest (K_1) rate.

The curve in Figure 5 is linear within experimental error at times greater than about ten hours and this linear portion of the curve yields a rate constant (K_2) of 2.75×10^{-2} hour⁻¹. However, this curve is very obviously not linear for run times of less than six hours. The linear portion of Figure 5 extrapolates back to about thirty-eight per cent of the remaining potassium (1.49 per cent of total potassium) at $t = 0$.

TABLE 1

TOTAL DISSOLUTION DATA FOR THE SAMPLES RUN AT 50°C

| Cumulative Time (Hours) | Sample 1 | | Sample 2 | |
|-------------------------------|---|------------------------|---|------------------------|
| | Cumulative K Removed (Milligrams) | % Total K Remaining | Cumulative K Removed (Milligrams) | % Total K Remaining |
| 0.0 | 0.0 | 100.00 | 0.0 | 100.00 |
| 0.25 | 0.98 | 98.82 | 0.94 | 98.86 |
| 0.50 | 1.20 | 98.55 | 1.14 | 98.62 |
| 0.75 | 1.31 | 98.42 | 1.25 | 98.49 |
| 1.0 | 1.38 | 98.33 | 1.33 | 98.39 |
| 1.5 | 1.48 | 98.21 | 1.43 | 98.27 |
| 2.0 | 1.60 | 98.07 | 1.52 | 98.16 |
| 3.0 | 1.74 | 97.90 | 1.68 | 97.97 |
| 4.0 | 1.89 | 97.72 | 1.84 | 97.78 |
| 5.0 | 2.03 | 97.55 | 1.99 | 97.59 |
| 6.0 | 2.17 | 97.38 | 2.17 | 97.38 |
| 10.0 | 2.60 | 96.86 | 2.55 | 96.92 |
| 20.0 | 3.12 | 96.23 | 3.15 | 96.19 |
| 30.0 | 3.63 | 95.62 | 3.68 | 95.55 |
| 42.0 | 4.31 | 94.80 | 4.39 | 94.69 |
| 66.0 | 5.22 | 93.70 | 5.29 | 93.60 |
| 90.0 | 6.09 | 92.65 | 6.23 | 92.47 |
| 114.0 | 6.81 | 91.78 | 7.03 | 91.50 |
| 138.0 | 7.50 | 90.95 | 7.85 | 90.51 |
| 162.0 | 8.20 | 90.10 | 8.71 | 89.47 |
| 186.0 | 8.95 | 89.20 | 9.53 | 88.48 |
| 210.0 | 9.69 | 88.30 | 10.35 | 87.48 |
| 234.0 | 10.29 | 87.58 | 11.05 | 86.64 |

Total Wt. Sample 1 10.0306 gm.

Total Wt. K in Sample 1 82.85 mg.

Total Wt. Sample 2 10.0118 gm.

Total Wt. K in Sample 2 82.70 mg.

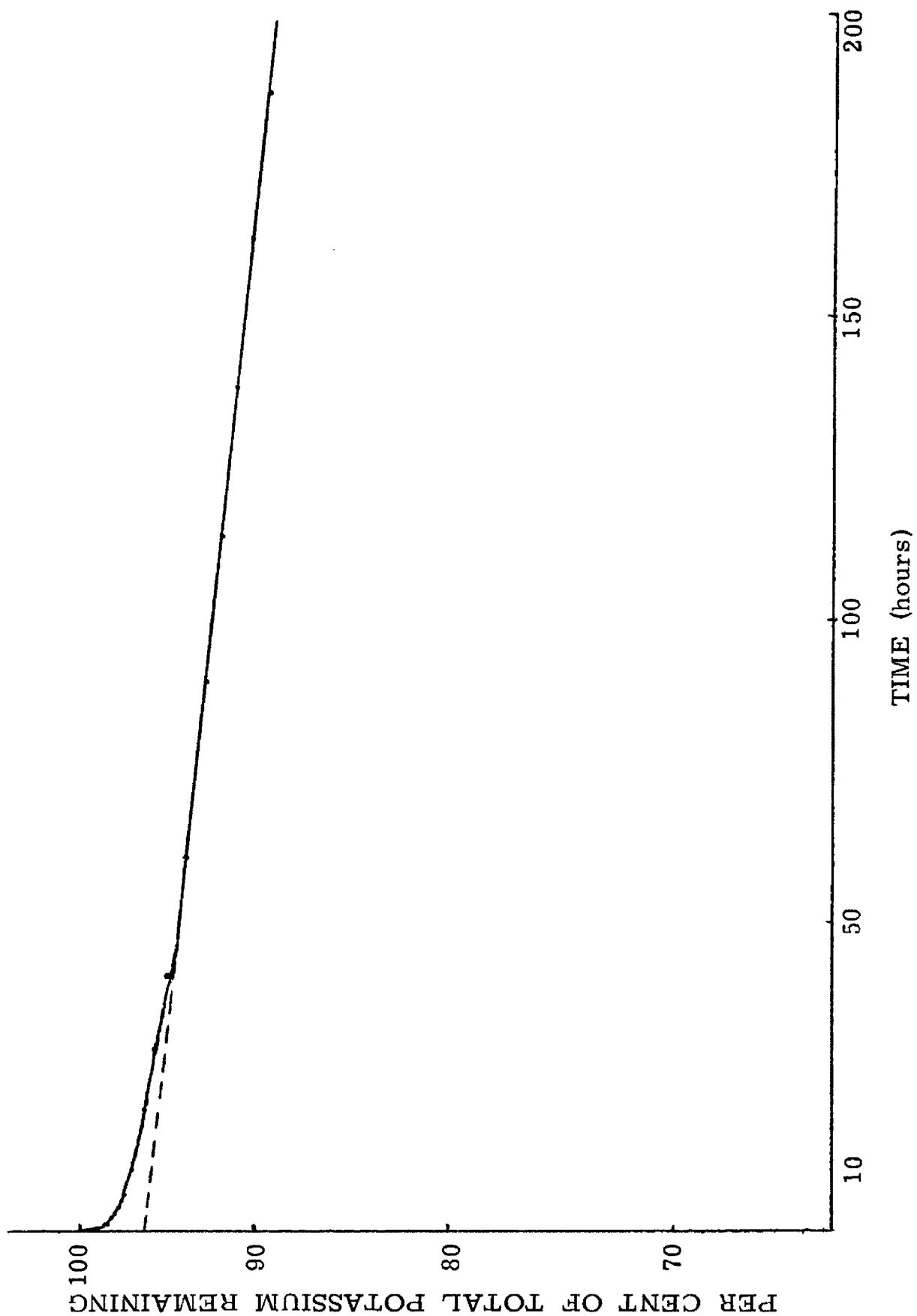


Fig. 4. --Total Potassium Dissolution Curve for Sample 1

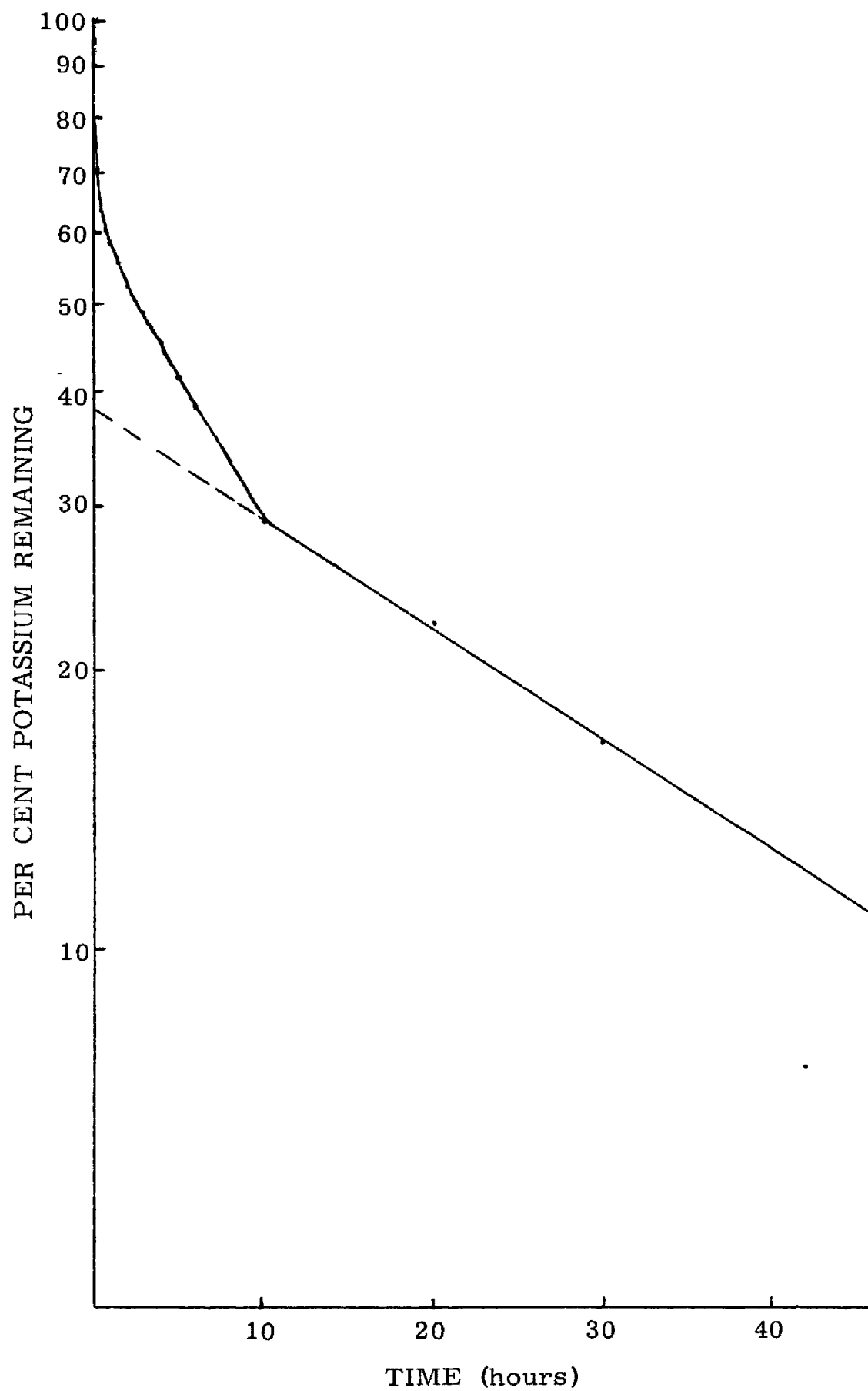


Fig. 5. --First Deconvolved Curve for Sample 1

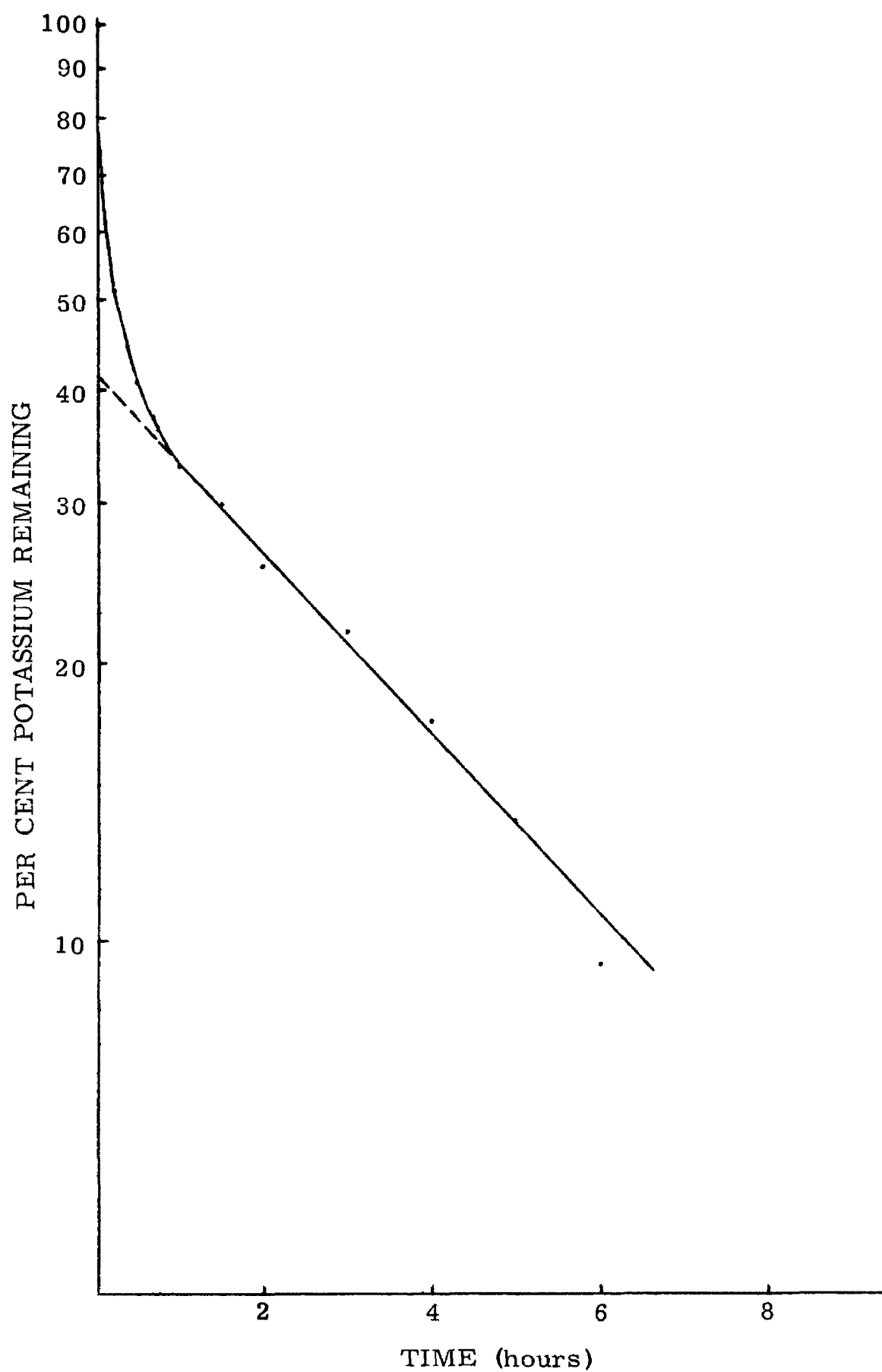


Fig. 6. --Second Deconvolved Curve for Sample 1

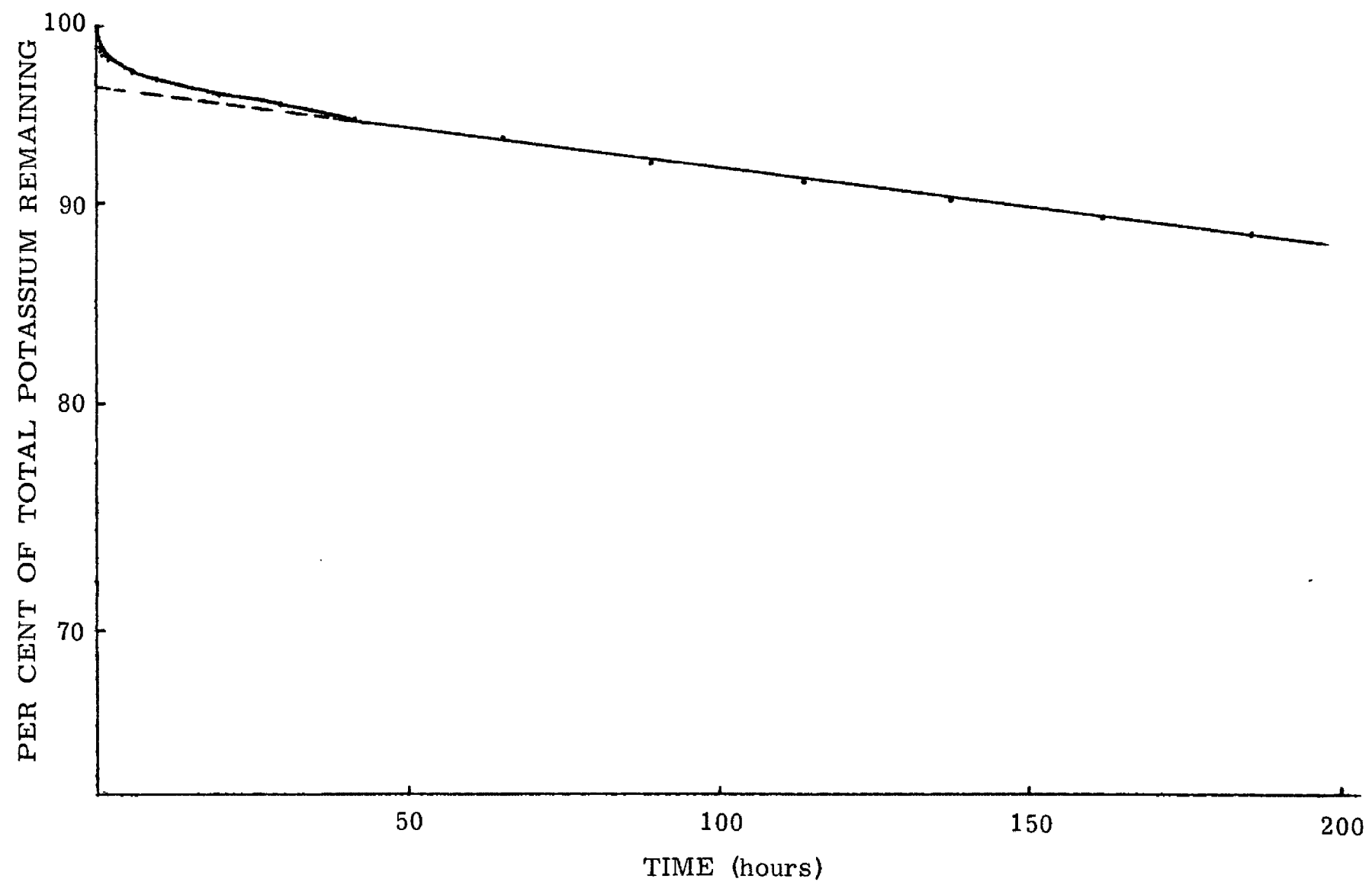


Fig. 7. --Total Potassium Dissolution Curve for Sample 2

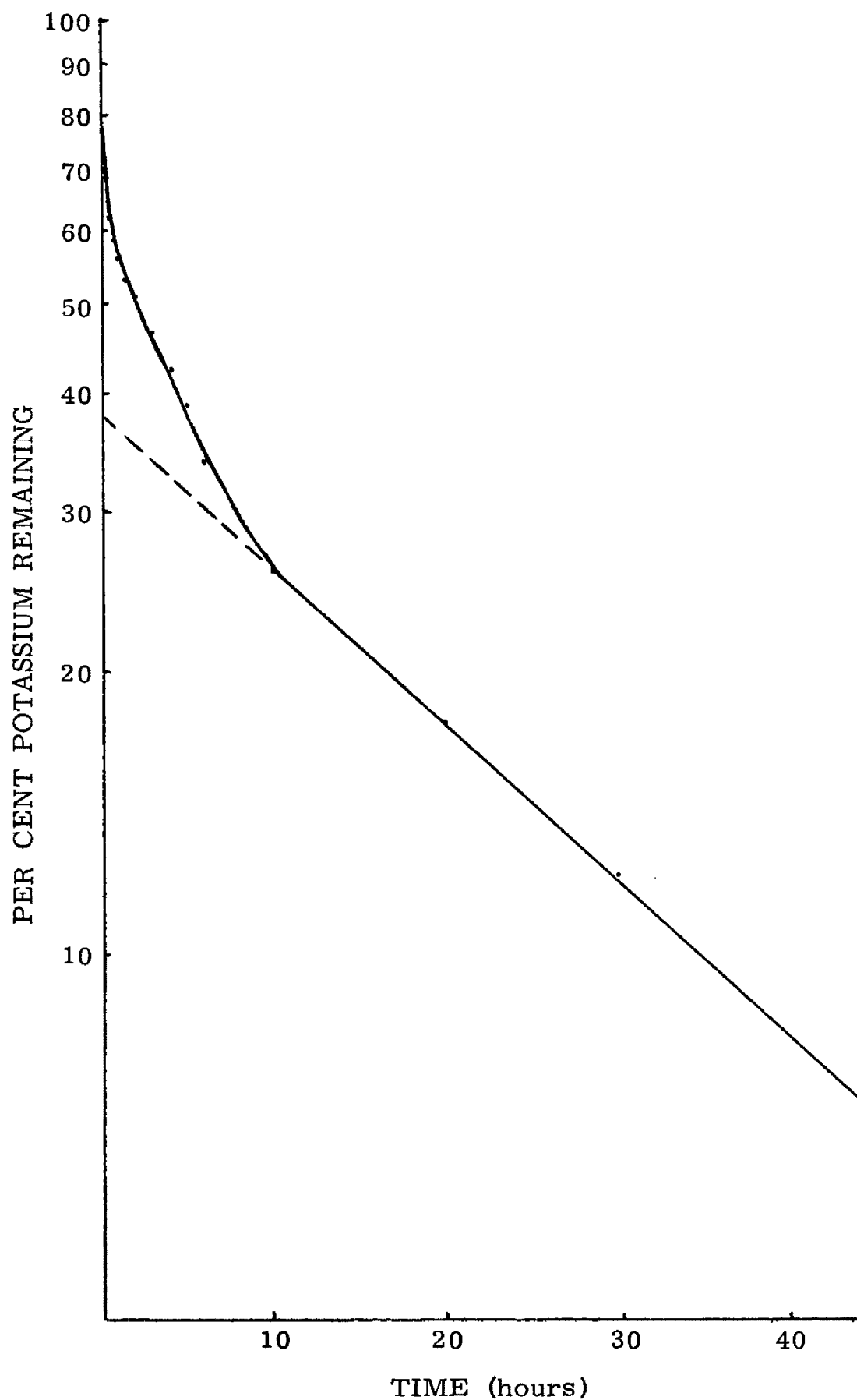


Fig. 8. --First Deconvolved Curve for Sample 2

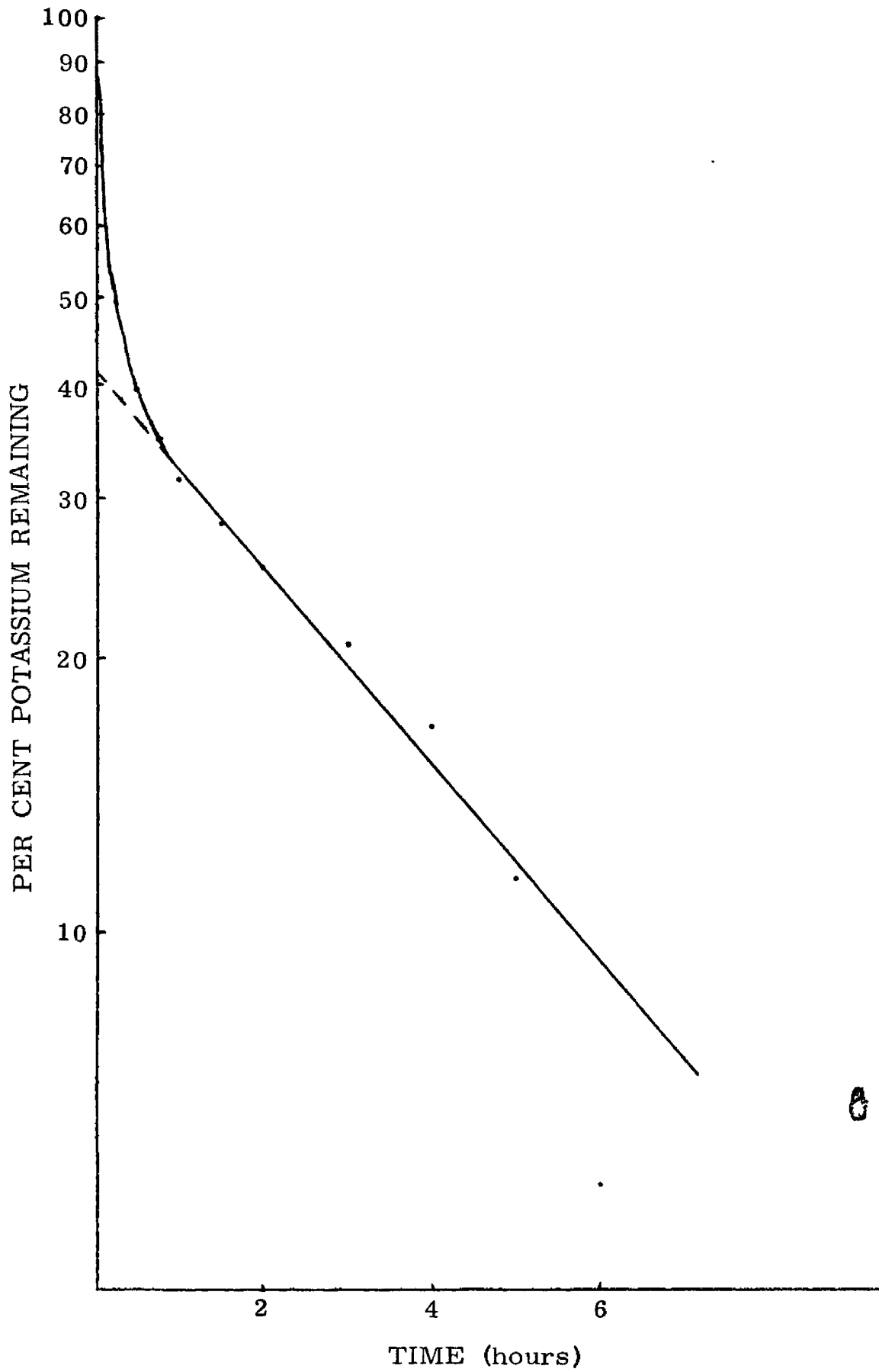


Fig. 9--Second Deconvolved Curve for Sample 2

Deconvolution of the curve in Figure 5 for times less than six hours yields the curve shown in Figure 6. This curve is again linear within experimental error at times greater than about .75 hours indicating that another first-order reaction controls removal of potassium at this third (K_3) rate. The rate constant (K_3) for this portion of the curve is $2.25 \times 10^{-1} \text{ hour}^{-1}$ and the linear portion extrapolates back to about forty-two per cent of the remaining potassium (1.0 per cent of the total potassium).

The remaining portion of the potassium was removed at an extremely rapid rate (K_4) which was calculated as 5.7 hour^{-1} . The potassium released at this rate was very loosely held and most of it was removed during the first exposure of the soil to the acid. Total potassium removed at this rate was 1.39 per cent.

Sample number two is a replicate of number one. Complete acid dissolution data for this sample is given in Table 1. The rate constants and percentage of the total potassium released at each rate is given in Table 3. Figure 7 shows the graph of total potassium removed, and Figures 8 and 9 show the first and second deconvolutions respectively. The data and the curves for Samples one and two are essentially identical.

The experiment was repeated on similar samples at a temperature of 80°C . Table 2 shows the complete results of the progressive acid dissolution of Samples 3 and 4 at 80°C . The results of the total

potassium extractions at this temperature are given by Figure 10 for Sample 3 and by Figure 13 for Sample 4. The results of these two samples are, again, so similar that I will only discuss Sample 3 as representative of both.

A comparison of this curve with that for the 50°C runs shows the same general form, but with a few differences. The major difference is that the slope of the linear portion of the curve is greater. The linear portion of this curve is interpreted as representing a first-order reaction with a rate constant (K_1) of $1.46 \times 10^{-3} \text{ hour}^{-1}$. Extrapolation of this line back to $t = 0$ shows that about ninety-two per cent of the soil's total potassium content is removed at the K_1 rate.

Deconvolution and normalization of the non-linear portion of Figure 10 for times less than about 40 hours yields the curve shown in Figure 11. The linear portion of this curve has a rate constant (K_2) of $4.71 \times 10^{-2} \text{ hour}^{-1}$ and extrapolation to $t = 0$ reveals that fifty-four per cent of the remaining potassium (4.17 per cent of the total potassium) was removed at this rate.

Deconvolution and normalization of the curve in Figure 11 yields the curve shown in Figure 12. This curve also has a linear portion, indicating a first-order reaction which has a rate constant (K_3) of $4.77 \times 10^{-1} \text{ hour}^{-1}$. Extrapolation of this portion to $t = 0$ shows that sixty-five per cent of the remaining potassium (2.31 per cent of the total potassium) was removed at this rate.

TABLE 2

TOTAL DISSOLUTION DATA FOR THE SAMPLES RUN AT 80°C

| Cumulative Time (Hours) | Sample 3 | | Sample 4 | |
|-------------------------------|---|------------------------|---|------------------------|
| | Cumulative K Removed (Milligrams) | % Total K Remaining | Cumulative K Removed (Milligrams) | % Total K Remaining |
| 0.0 | 0.0 | 100.00 | 0.0 | 100.00 |
| 0.25 | 1.18 | 98.57 | 1.22 | 98.53 |
| 0.50 | 1.54 | 98.14 | 1.58 | 98.09 |
| 0.75 | 1.81 | 97.81 | 1.84 | 97.78 |
| 1.0 | 2.00 | 97.58 | 2.05 | 97.52 |
| 1.5 | 2.41 | 97.08 | 2.37 | 97.14 |
| 2.0 | 2.73 | 96.70 | 2.62 | 96.84 |
| 3.25 | 3.24 | 96.08 | 3.06 | 96.31 |
| 4.0 | 3.60 | 95.65 | 3.36 | 95.94 |
| 5.0 | 4.02 | 95.14 | 3.72 | 95.51 |
| 6.0 | 4.38 | 94.70 | 4.01 | 95.16 |
| 7.0 | 4.72 | 94.29 | 4.31 | 94.80 |
| 15.0 | 6.10 | 92.62 | 5.57 | 93.27 |
| 18.0 | 6.67 | 91.93 | 6.15 | 92.57 |
| 22.0 | 7.39 | 91.06 | 6.94 | 91.62 |
| 26.0 | 8.08 | 90.23 | 7.93 | 90.43 |
| 30.0 | 8.81 | 89.34 | 8.73 | 89.46 |
| 38.0 | 10.02 | 87.88 | 9.85 | 88.11 |
| 42.0 | 10.78 | 86.96 | 10.52 | 87.30 |
| 66.0 | 13.44 | 83.74 | 12.84 | 84.50 |
| 90.0 | 15.90 | 80.77 | 15.26 | 81.57 |
| 114.0 | 18.16 | 78.03 | 17.37 | 79.03 |
| 138.0 | 20.40 | 75.32 | 19.55 | 76.39 |
| 162.0 | 22.33 | 72.99 | 21.35 | 74.22 |
| 188.0 | 24.53 | 70.33 | 23.30 | 71.87 |
| 210.0 | 26.43 | 68.03 | 24.96 | 69.86 |
| 234.0 | 28.13 | 65.97 | 26.64 | 67.83 |

Total Wt. Sample 3 10.0090 gm. Total Wt. K in Sample 3 82.67 mg.

Total Wt. Sample 4 10.0261 gm. Total Wt. K in Sample 4 82.82 mg.

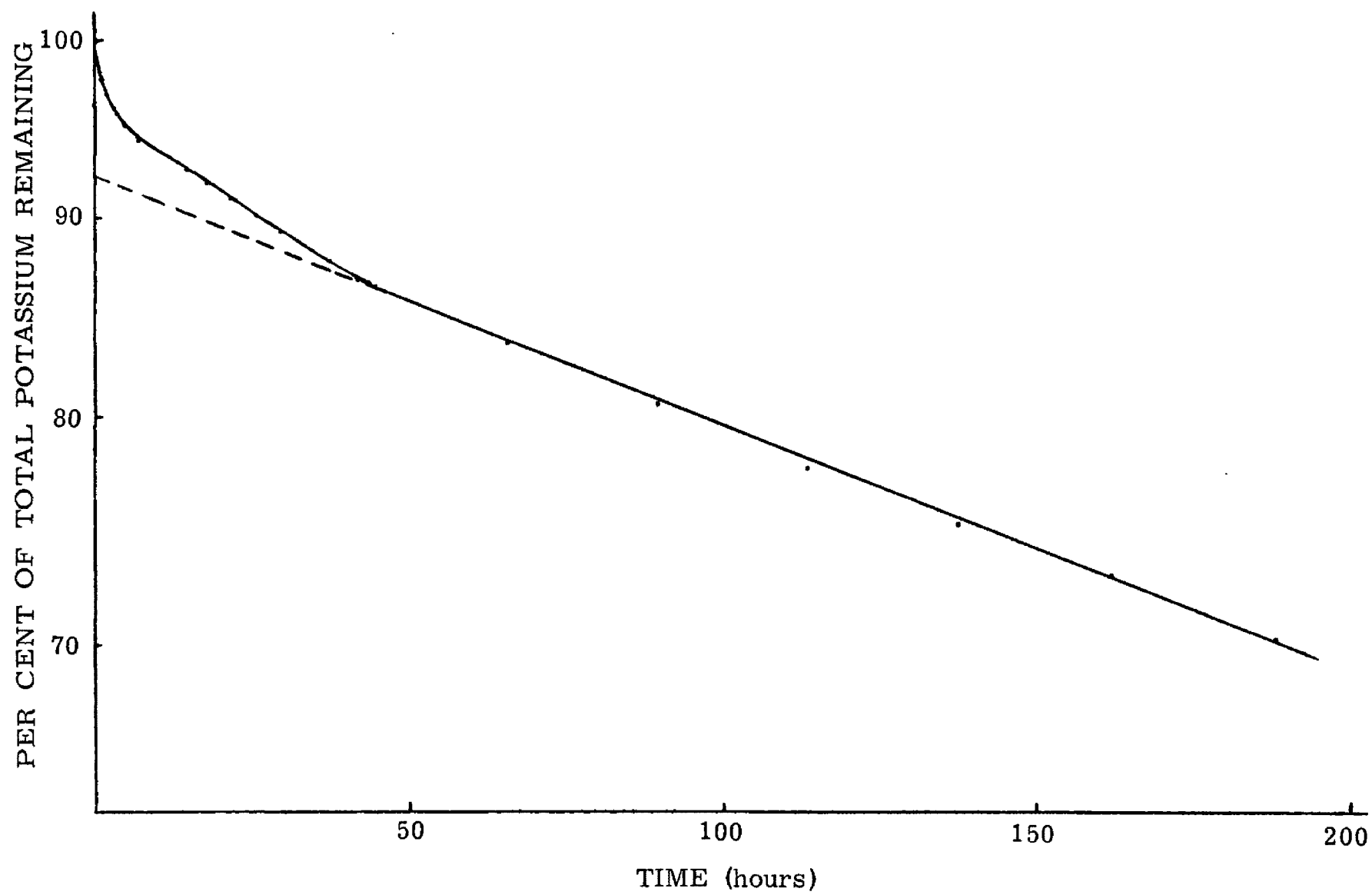


Fig. 10. --Total Potassium Dissolution Curve for Sample 3

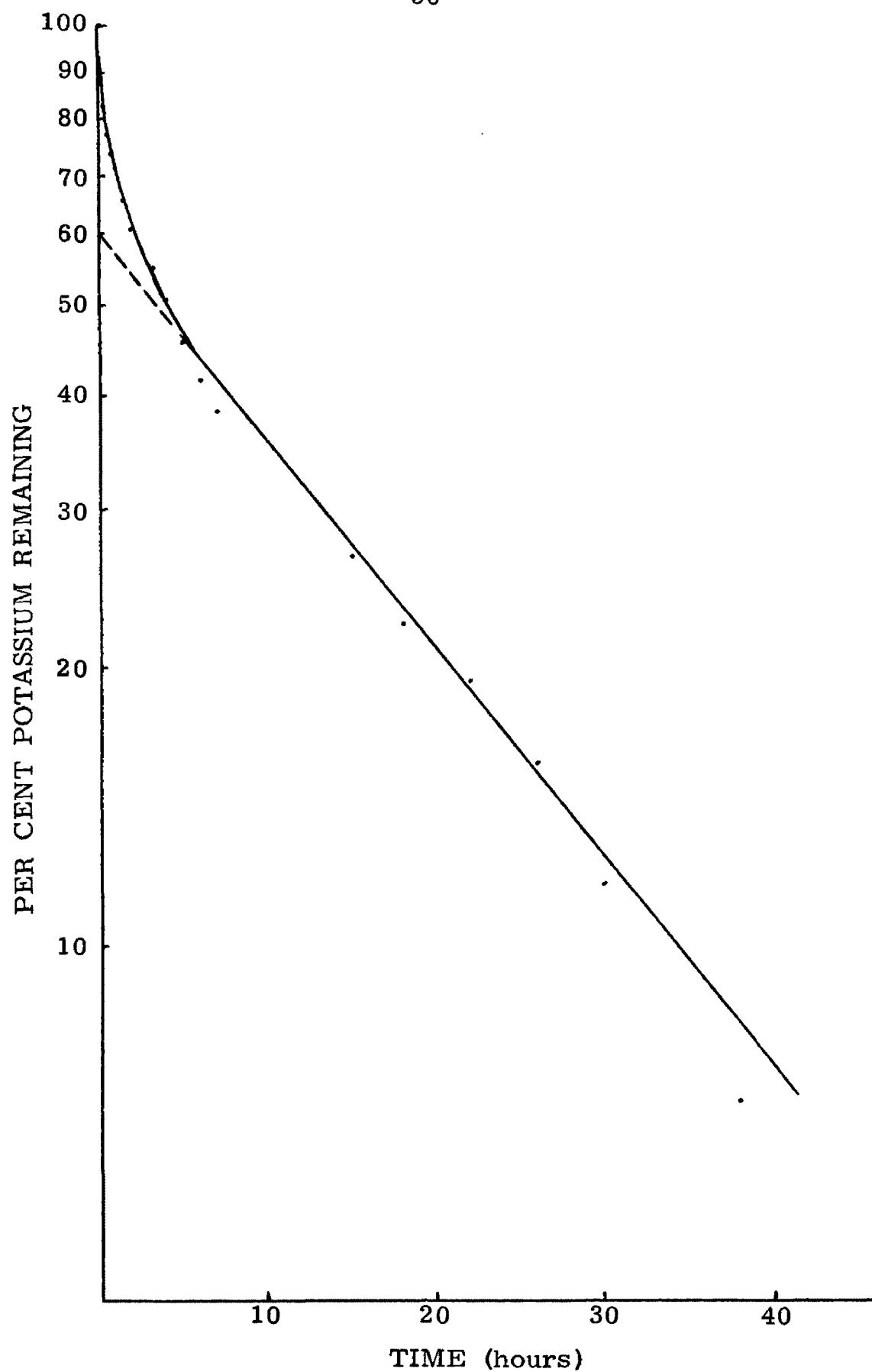


Fig. 11. --First Deconvolved Curve for Sample 3

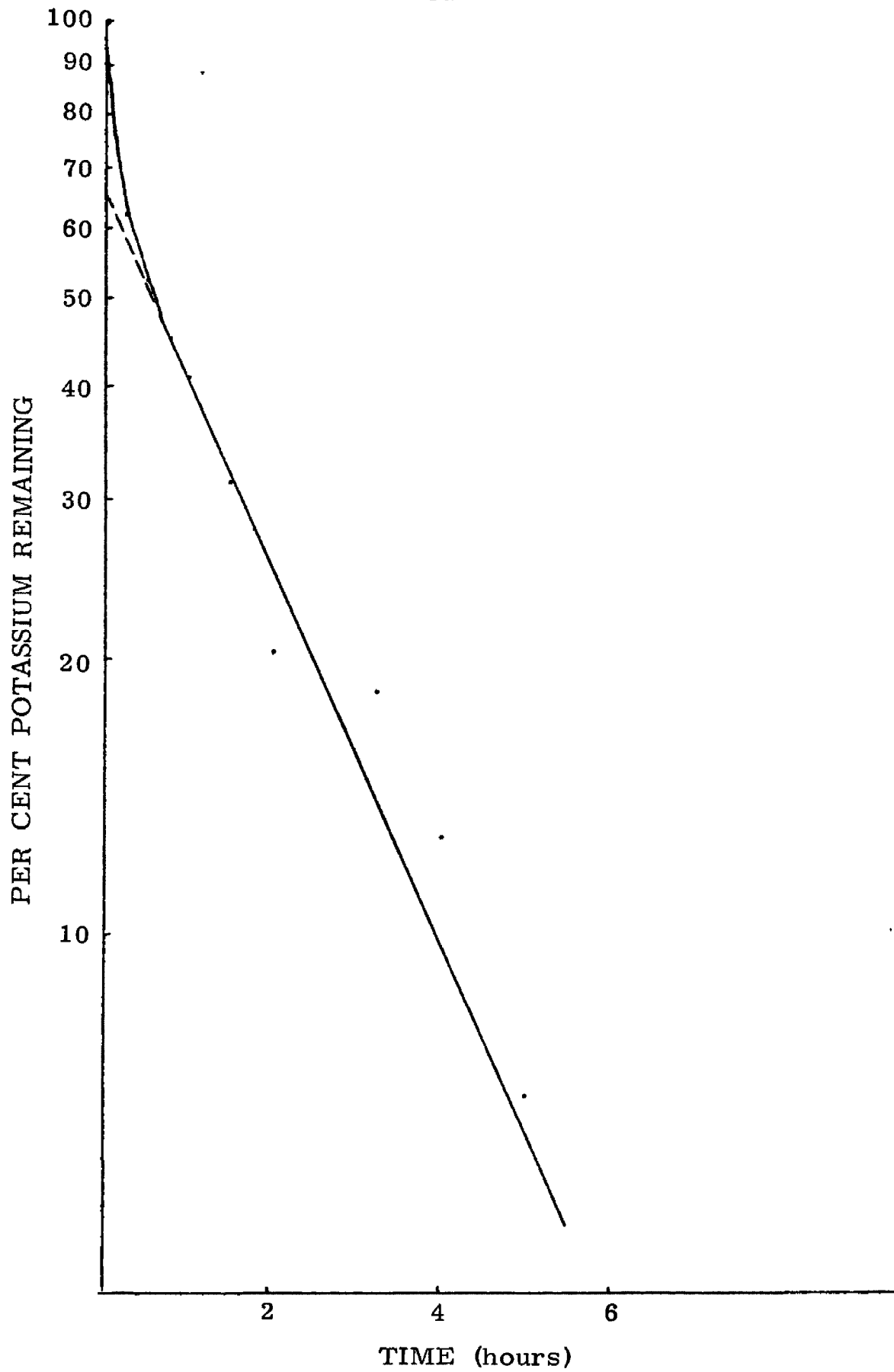


Fig. 12. --Second Deconvolved Curve for Sample 3

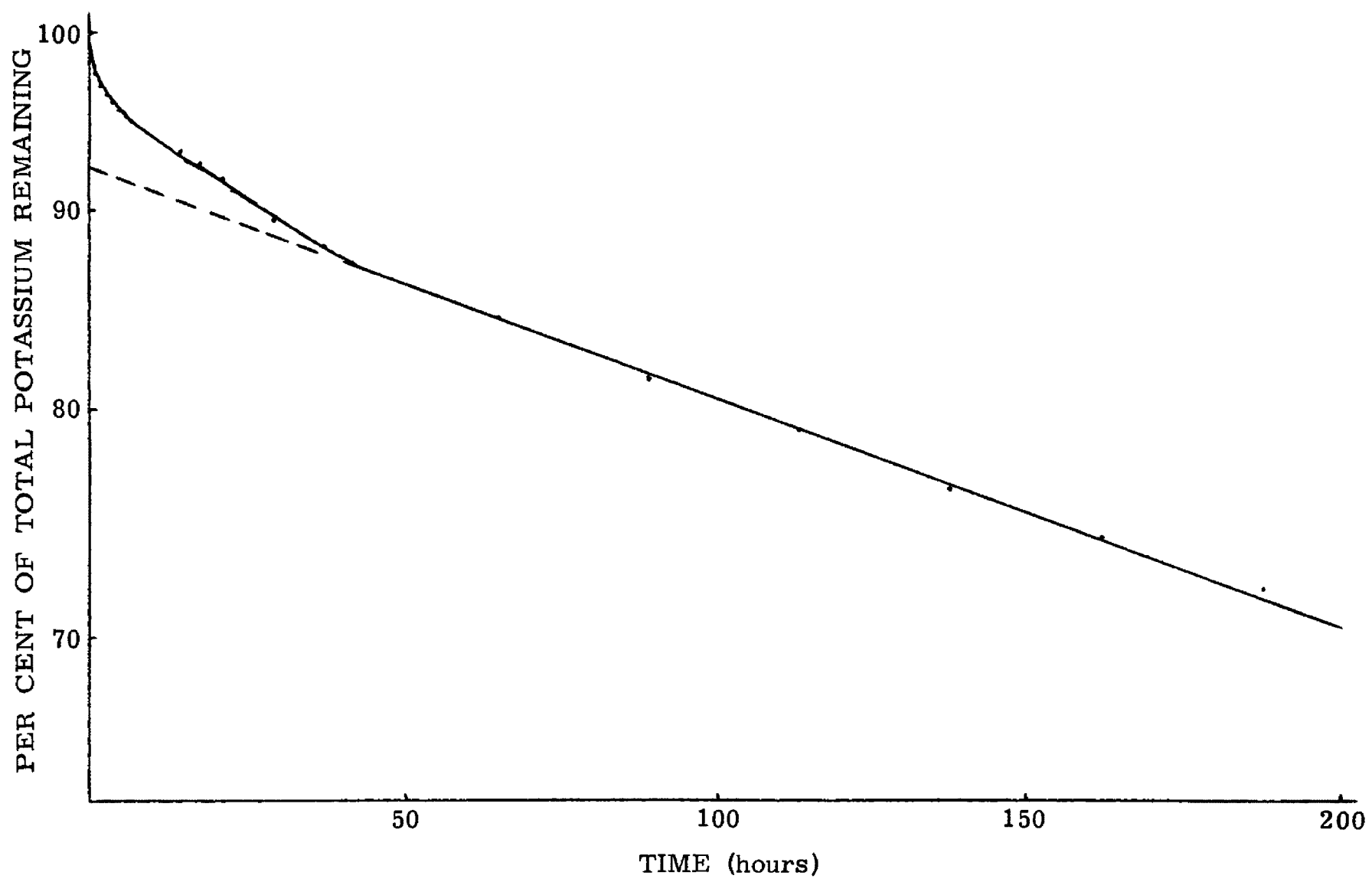


Fig. 13. --Total Potassium Dissolution Curve for Sample 4

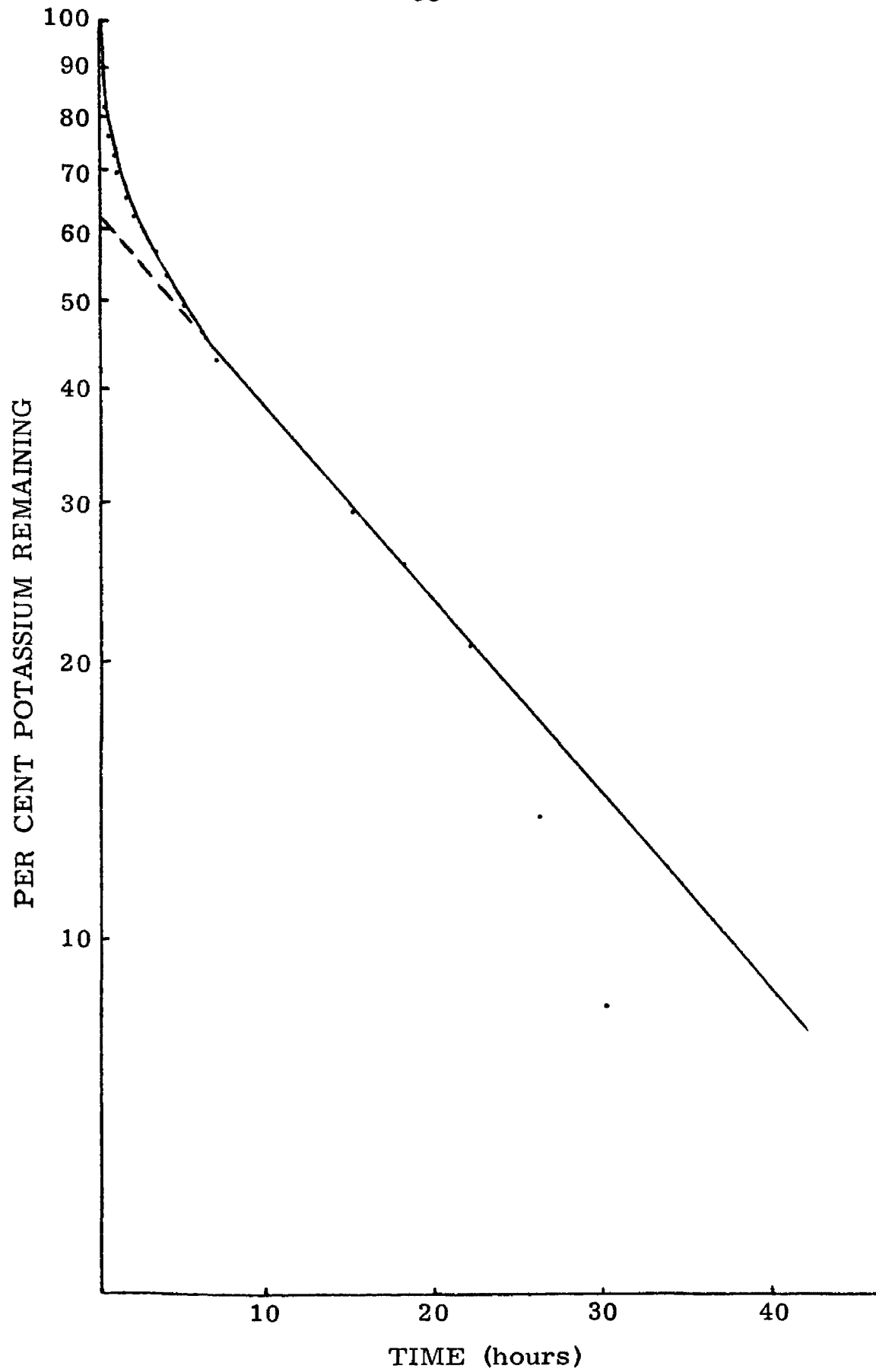


Fig. 14. --First Deconvolved Curve for Sample 4

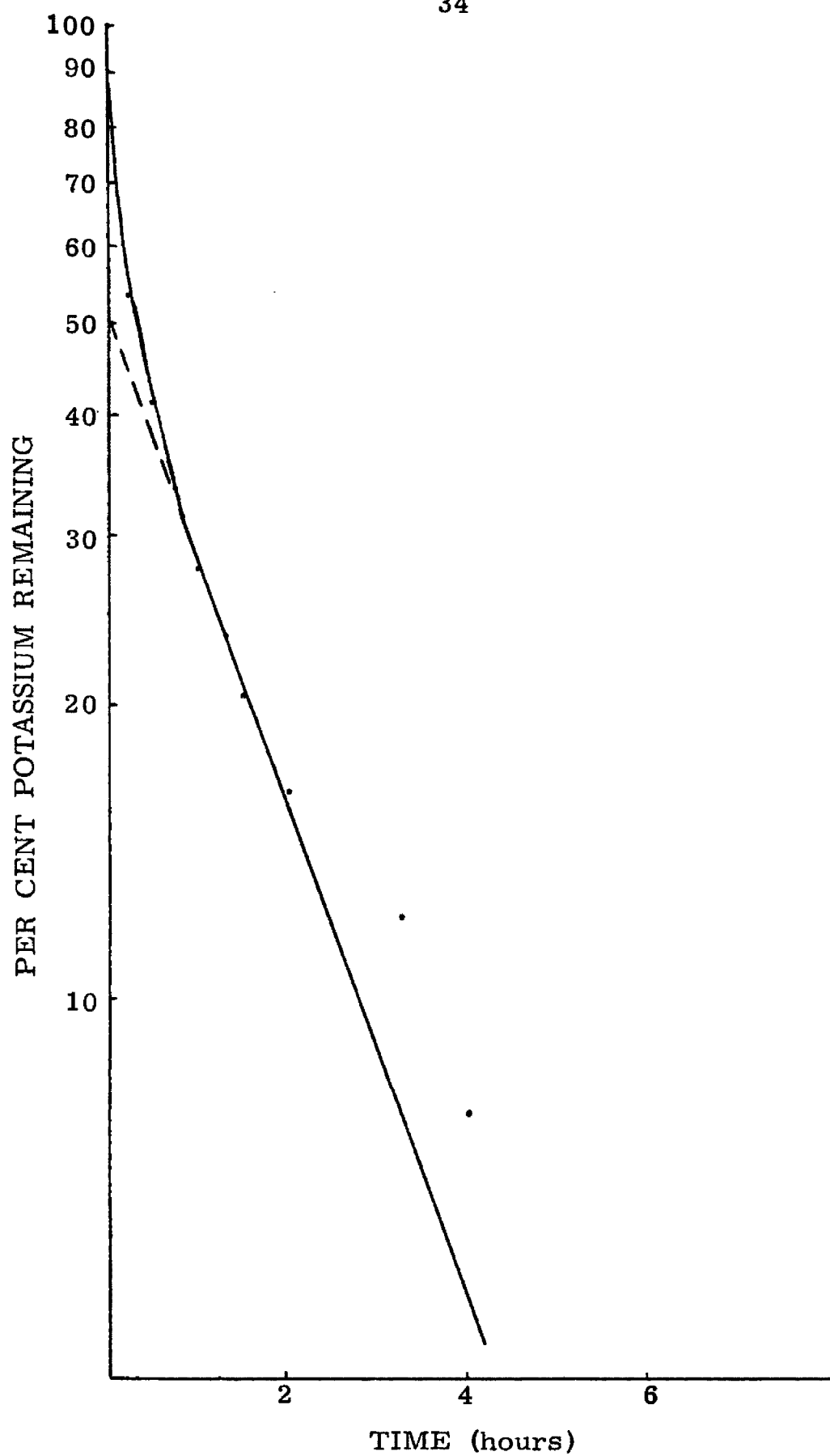


Fig. 15. --Second Deconvolved Curve for Sample 4

The remaining potassium was removed quite rapidly by the acid. The rate for this reaction was calculated as 7.28 hour^{-1} . Total potassium removed at this rate was 1.24 per cent.

The total progressive acid dissolution curve of Sample 4 and the first and second deconvolutions of the total potassium dissolution curve are shown in Figures 13, 14, and 15.

Thus in all the samples subjected to progressive acid dissolution there appear to be four different rates at which potassium is removed. These four first-order reactions appear to indicate the presence of four sites at which potassium is held in the soil.

By assuming that the four rates found at 50°C and the four rates found at 80°C represent the same four bond sites it is possible to calculate activation energies for the reactions. The Arrhenius equation which is used to calculate activation energies is:

$$K = Ae^{-E/RT}$$

where

K = rate constant

A = constant

E = activation energy in calories
per mole

R = gas constant

T = absolute temperature

(Moore, 1962)

The working form of the Arrhenius equation is:

$$E = \frac{R(\Delta \ln K)}{\Delta \left(\frac{1}{T} \right)}$$

(Thompson, 1971)

The two 50°C runs were averaged and the two 80°C runs were averaged as shown in Table 3, and the average values for rate constants thus obtained were used to calculate the activation energies for the four reactions. The activation energy for the potassium removed at the slowest rate (K_1) is 8.93 Kcal mole⁻¹, the activation energy for the K_2 rate is 2.87 Kcal mole⁻¹, the activation energy for the K_3 rate is 6.10 Kcal mole⁻¹, and the activation energy for the most rapid rate (K_4) is 0.69 Kcal mole⁻¹.

Another comparison which can be made between the 50°C runs and those made at 80°C is between the percentages of total potassium held at each type of site and therefore held with the same activation energy. These comparisons can be made by examining the data in Table 3. For instance, the potassium removed at the slowest rate in the 50°C runs was calculated to be about ninety-six per cent of the total potassium. This is in comparison to the 80°C runs for which the total potassium removed at the slowest rate was calculated to be ninety-two per cent. There are also differences between the percentages of total potassium removed at the K_2 and K_3 rates at 50°C and the corresponding

TABLE 3

PERCENTAGES OF TOTAL POTASSIUM, RATE CONSTANTS, AND ACTIVATION ENERGIES
FOR THE FOUR CALCULATED RATES OF REMOVAL

| Item | Rate K_1 | | Rate K_2 | | Rate K_3 | | Rate K_4 | |
|---|--------------|----------------------------|--------------|----------------------------|--------------|----------------------------|--------------|----------------------------|
| | % Total K | K_1 (hr. ⁻¹) | % Total K | K_1 (hr. ⁻¹) | % Total K | K_1 (hr. ⁻¹) | % Total K | K_4 (hr. ⁻¹) |
| 50°C | | | | | | | | |
| Sample 1 | 96.12 | 4.01×10^{-4} | 1.49 | 2.75×10^{-2} | 1.00 | 2.25×10^{-1} | 1.39 | 5.70 |
| Sample 2 | 96.44 | 4.62×10^{-4} | 1.35 | 3.76×10^{-2} | 0.92 | 2.45×10^{-1} | 1.29 | 5.87 |
| Avg. of 1 & 2 | 96.28 | 4.32×10^{-4} | 1.42 | 3.26×10^{-2} | 0.96 | 2.35×10^{-1} | 1.34 | 5.79 |
| 80°C | | | | | | | | |
| Sample 3 | 92.28 | 1.46×10^{-3} | 4.17 | 4.71×10^{-2} | 2.31 | 4.77×10^{-1} | 1.24 | 7.28 |
| Sample 4 | 92.38 | 1.36×10^{-3} | 4.66 | 4.83×10^{-2} | 1.51 | 5.77×10^{-1} | 1.45 | 5.39 |
| Avg. of 3 & 4 | 92.33 | 1.41×10^{-3} | 4.42 | 4.77×10^{-2} | 1.89 | 5.27×10^{-1} | 1.36 | 6.34 |
| Activation Energy (Kcal. mole ⁻¹) | | | | | | | | |
| Activation Energy | 8.93 | | 2.87 | | 6.10 | | 0.69 | |

percentages calculated for the 80°C runs. However, there is very good agreement between the percentages removed at the fastest (K_4) rate at 50°C (1.34 per cent of total potassium) and the corresponding figure for the 80°C runs (1.36 per cent of total potassium).

The similarity between these last two values probably indicates that an actual reservoir of potassium in the soil containing about 1.35 per cent of the total potassium exists. This reservoir appears to be more discrete than the others because the relative amounts of the total potassium removed at rates K_1 , K_2 , and K_3 showed variation with the temperature of the reaction. No such variation with temperature existed for the potassium removed at the K_4 rate.

The apparent variation with temperature seen between the potassium removed at rates K_1 , K_2 , and K_3 is indication that the sites of potassium storage in the soil associated with these rates may not be discrete. For example, the potassium removed at rate K_2 at 80°C might include the potassium held at hypothetical sites X and Y in the soil while at 50°C, site X appears to be removed at rate K_2 , but site Y is included with the potassium removed at rate K_1 . The possibility of such an occurrence exists due to the fact that soil is composed of such a variety of types of minerals, many of which might actually have different, but very similar, energies with which they hold potassium. The precision of the progressive acid dissolution technique may not be great enough to detect such small differences. Additional refinement

of the technique might help clarify this apparent lack of precision, but even without further clarification the data gives good insight into potassium relationships in this soil. The meaning of this data will be considered in the Discussion chapter.

The curves in Figures 11 and 14 were corrected at the 15, 18, 22, 26, and 30 hour extraction time intervals by lowering the values of per cent remaining. This correction was made because the temperature of the water bath for at least part of this time was too low. The low temperature decreased the rate of potassium removal during this period giving points for percentage remaining that were too high. The results obtained without correction were entirely unreasonable. The low values for activation energy obtained for this rate (K_2) was probably also due to the low temperature.

This problem may also have created an artificially low value for the slope of the line in Figures 11 and 14. The low value for these rate constants is probably at least a partial cause of the low value for the activation energy calculated for rate K_2 . The relationship between the calculated activation energies of the K_2 and K_3 rates cannot possibly reflect the true situation. The activation energy for the K_2 reaction must be higher than that of the K_3 reaction, since the rate constants for the K_2 reaction are lower than those for the K_3 reaction.

Another possible explanation for this anomaly is the same one given for the difference that temperature made in determining the

percentage of total potassium removed at each rate. If there exist more rates (and therefore more sites of potassium storage) than the experiment was able to detect, then the straight lines used in the deconvolutions are not representative of the actual situation, but only of the data collected, and the secondary calculations made from the data are not valid.

CHAPTER V

DISCUSSION

A major purpose of this thesis was to determine whether progressive acid dissolution is a technique which can be applied to determination of the characteristics of the potassium reservoir of a forest soil. More particularly, it was hoped that this technique would be able to detect the relative rates of release of potassium from various forms in the soil and to measure the size of the reservoir held in each of these forms, information which would be of value in studies of nutrient cycling.

The results obtained indicate that progressive acid dissolution can be successfully applied to soils. The form of the results obtained (a curve showing the decrease in extraction rate of potassium with increasing time of exposure to acid) is readily interpretable in terms of several simultaneous dissolution reactions. The results are somewhat ambiguous when one attempts to attribute each reaction to removal of potassium from a discrete site within the soil. This ambiguity is probably due to the multiplicity of such sites in this soil. However, a general interpretation of the results in terms of sites at which potassium is bound can be made.

For the Everett Soil from the Allen E. Thompson Research Center in the Cedar River watershed, the following conclusions can be made. There are very roughly four different sites at which potassium is bound in this soil. The least tightly bound potassium was released at the most rapid rate and consisted of about 1.35 per cent of the total potassium present in this soil. This fraction of total potassium is roughly equivalent to the potassium exchangeable with pH 7.1 normal ammonium acetate which was determined as being in the range of .8 to .9 per cent of the total potassium in this soil. The 1.35 per cent of total potassium removed at the most rapid rate probably corresponds to that adsorbed as ions on the surfaces of mineral and organic particles in the soil, and as such represented that portion of the soil's total potassium which is directly and immediately available to plants.

The potassium removed at the slowest rate (K_1) is also fairly easy to characterize as to the site in the soil it occupies. It was removed at the slowest rate, constituted something in excess of ninety per cent of the total soil potassium, and was most probably equivalent to the potassium held in lattice sites in primary and secondary minerals. Schlichte (1968) noted that most of the potassium found in this soil is found in the potassium feldspars. This potassium fraction is so tightly bound as to be only very slowly released, probably by weathering of the soil on a geologic time scale. Thus, this fraction would only provide significant contribution to the potassium cycling in this ecosystem when measured over geologic time.

The remaining potassium, constituting somewhere in the neighborhood of three to seven per cent of the total potassium, is bound with an energy intermediate between the two extreme forms, and is probably bound in two or more forms within the soil. Any attempt at designating a particular binding site for this potassium fraction can be nothing more than speculation. However, some possibilities which exist are that it might be chelated by organic compounds or held between hydrated layers of layer silicates but sunken to the level of the basal oxygens. In studies on the clay fraction of another soil Bolt, et al. (1963) and Voigt (1963) interpreted intermediately bound potassium as being potassium ions held in interlayer sites near the surfaces of particles.

The role which this intermediately bound potassium plays with respect to nutrient cycling may be a key one. One possible scheme which seems reasonable and which has some interesting consequences is as follows. The intermediately held potassium, being in equilibrium with the exchangeable is the immediate source of the potassium which replenishes whatever exchangeable potassium is removed through absorption by plants, leaching, etc. Under normal circumstances when a climax ecosystem occupies the site, this form of potassium would only be slowly released. Under such circumstances, cycling of potassium within the ecosystem would not require drawing on this reservoir except at a low rate equivalent to loss of

potassium from the system, and equivalent to the rate of release of potassium from silicate lattices by weathering, and it would remain essentially constant. However, if the site were logged and a portion of the ecosystem's potassium supply removed as lumber, the balance would be upset. Erosion and increased run-off can also reduce the potassium reservoir of an ecosystem, but in this case by removal of soil clays and silts. Cole and Gessel (1963) clear-cut a one-tenth acre plot and analyzed leachates collected in tension lysimeters. They found only a six per cent increase in potassium leached beyond the rooting zone. Even though leaching is apparently not a significant drain on the ecosystem's potassium reservoir, removal of wood and bark would remove from the ecosystem an amount of potassium comparable in magnitude with that held in exchangeable form. In the next growth of timber this potassium would have to be made up from that held in intermediately bound forms. The intermediate forms might be sufficient to replace available potassium a few times, but given the size of this reservoir (about three to seven per cent of total potassium or about 700 to 1700 kilograms/hectare) it would become exhausted after a relatively few such events. At this point the availability of potassium would become controlled by the relatively slow weathering of potassium-bearing minerals. Consequently, there would be a reduction in site quality and the relatively rapid return of a climax forest associated with secondary succession could not be expected to

occur. A similar, but shorter ranged reduction in fertility by intensive cropping is well known in annual crop agriculture.

If the intermediately bound potassium is combined with the exchangeable potassium and assumed to represent the reservoir of soil potassium involved in cycling the supply of potassium in the soil is at least quadrupled. This helps to resolve the problem evident when considering the data from Cole, Gessel, and Dice (1967). Using exchangeable potassium to represent the soil's entire supply, they calculated that at present rates of demand this reservoir would be depleted by twelve years growth. At the time Cole, Gessel, and Dice (1967) measured annual uptake of nutrients, the trees (at age thirty-six) were in their period of most rapid growth. Based on the expected future growth of Douglas fir in the Pacific Northwest region (McArdle, 1930), these trees cannot be expected to continue to absorb nutrients at the rate measured. This is particularly true since amount of foliage, which contains the largest fraction of potassium of all components of the tree (Cole, Gessel, and Dice, 1967), can be expected to remain relatively constant from this point on in the tree's life history. Thus a decreased rate of nutrient uptake and an increased estimate of soil potassium reservoir make the cycle of potassium in this ecosystem appear more reasonable, probably adequate, considering the combined compartments, to permit this second-growth stand to reach maturity without an external potassium source. This appears to be generally

the case, as growth response following potassium fertilization in the northwest are relatively uncommon observations (Cole, personal communication). However, the results of this study do suggest that potassium fertilization may become an increasingly necessary activity to maintain the fertility required for future growth on soils such as the Everett series.

REFERENCES

- Bolt, G. H., Summer, M. E., and Kamphorst A. 1963. A Study of the Equilibrium Between Three Categories of Potassium in an Illitic Soil. Proceedings of the Soil Science Society of America. 27:294-299.
- Bormann, F. H., and Likens, G. E. 1967. Nutrient Cycling. Science. 55:424-429.
- Cole, Dale W., Associate Professor of Forest Soils, College of Forest Resources, University of Washington. Personal communication.
- _____, and Ballard, T. M. 1970. Mineral and Gas Transfer in a Forest Floor--A Phase Model Approach. Pp. 347-353 in Tree Growth and Forest Soils. Edited by Chester T. Youngberg and Charles B. Davey. Corvallis: Oregon State University Press.
- _____, and Gessel, Stanley P. 1963. Movements of Elements Through a Forest Soil as Influenced by Tree Removal and Fertilizer Additions. Pp. 95-104 in Forest Soil Relationships in North America. Edited by Chester T. Youngberg. Corvallis: Oregon State University Press.
- _____, and Gessel, Stanley P. 1968. Cedar River Research--A Program for Studying the Pathways, Rates, and Processes of Elemental Cycling in a Forest Ecosystem. Forest Resources Monograph. Contribution No. 4. Institute of Forest Products, University of Washington College of Forest Resources.
- _____, Gessel, S. P., and Dice, S. F. 1967. Distribution and Cycling of Nitrogen, Phosphorus, Potassium, and Calcium in a Second-Growth Douglas-Fir Ecosystem. Pp. 198-213 in Symposium on Primary Productivity and Mineral Cycling in Natural Ecosystems. Ecological Society of America. University of Maine Press.
- Fried, Maurice and Broeshart, Hans. 1967. The Soil-Plant System. New York and London: Academic Press.

- Garmon, W. L. 1957. Potassium Release Characteristics of Several Soils from Ohio and New York. Proceedings of the Soil Science Society of America. 21:52-58.
- Gessel, Stanley P. and Cole, Dale W. 1965. Influence of Removal of Forest Cover on Movement of Water and Associated Elements Through Soil. Journal American Water Works Association. 57:1301-1310.
- Grier, Charles C. and Cole, Dale W. 1971. Influences of Slash Burning on Ion Transport in a Forest Soil. Northwest Science. 45:100-106.
- Hood, J. T., Brady, N. C., and Lathwell, D. J. 1956. The Relationship of Water Soluble and Exchangeable Potassium to Yield and Potassium Uptake by Ladino Clover. Proceedings of the Soil Science Society of America. 20:228-231.
- Jackson, Marion L. 1964. Chemical Composition of Soils. Pp. 71-241 in Chemistry of the Soil, second edition. Edited by Firman E. Bear. American Chemical Society Monograph Series. New York: Rheinhold Publishing Corporation.
- Leaf, Albert L. 1968. K, Mg, and S Deficiencies in Forest Trees. Pp. 88-122 in Forest Fertilization, Theory and Practice. Papers presented at the Symposium on Forest Fertilization, April 1967 at Gainesville, Florida. Muscle Shoals, Alabama: Tennessee Valley Authority National Fertilizer Development Center.
- McArdle, Richard E. 1930. The Yield of Douglas Fir in the Pacific Northwest. United States Department of Agriculture Technical Bulletin No. 201. Washington, D.C.: U.S. Dept. of Agriculture.
- McColl, John Graham. 1969. Ion Transport in a Forest Soil: Models and Mechanisms. Unpublished Ph.D. thesis, University of Washington.
- _____, and Cole, D. W. 1968. A Mechanism of Cation Transport in a Forest Soil. Northwest Science. 42:134-140.
- Moore, Walter J. 1962. Physical Chemistry. Englewood Cliffs, N.J.: Prentice-Hall Inc.

- Nelson, L. E. 1959. A Comparison of Several Methods for Evaluating the Potassium Status of Some Mississippi Soils. Proceedings of the Soil Science Society of America. 23:313-316.
- Pratt, R. F., Simon, R. H., and Volk, G. W. 1956. Release of Potassium from Nonexchangeable Forms in Relation to Soil Reaction. Proceedings of the Soil Science Society of America. 20:190-192.
- Reitemeier, R. F. 1951. Soil Potassium. Pp. 113-164 in Advances in Agronomy, Vol. III. Edited by A. G. Norman. New York: Academic Press.
- Salomon, Milton and Smith, John B. 1957. A Comparison of Methods of Determining Extractable Soil Potassium in Fertilizer Test Plots. Proceedings of the Soil Science Society of America. 21:222-225.
- Schlichte, A. Kenneth. 1968. The Mineralogy of the Everett Soil Series at the Cedar River Watershed. Unpublished M. S. F. thesis, University of Washington.
- Schmitz, G. W. and Pratt, P. F. 1953. Exchangeable and Nonexchangeable Potassium as Indexes to Yield Increase and Potassium Absorption by Corn in the Greenhouse. Soil Science. 76:345-353.
- Thompson, Graham R. 1971. The Crystal-Chemistry of Glauconite: An Explanation for Low Radiometric Ages from Glauconites. Unpublished Ph.D. dissertation, Case Western Reserve University.
- Voigt, G. K. 1963. Biological Mobilization of Potassium from Primary Minerals. Pp. 33-46 in Forest Soil Relationships in North America. Edited by Chester T. Youngberg. Corvallis: Oregon State University Press.