

A Fundamental Study on the Infiltration Characteristics of Radioactive Liquid Wastes

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Abstract

When a radioactive liquid waste, containing some radioactive substance, is released or leaked from a plant using atomic energy or nuclear products and spread over the the ground surface in that place, it will percolate into the soil and an adsorbable substance contained in the liquid will be partly adsorbed by soil particles. As one of the fundamental studies on this problem, we discussed the motion of liquid through unsaturated porous media, then introduced a theory to estimate the variation of the concentration of radioactive substance in the flowing liquid. Furthermore, the validity of this theory was verified qualitatively by laboratory experiments with a filter column.

1. Introduction

Generally, since the behaviour of various radioactive substances in a wasted liquid, flowing through porous media, is governed by the adsorption capacity of the medium layer, these substances ordinarily appear somewhat later than the wet front of solvent at the lower part of the layer. Therefore, in order to estimate the local- and time-fluctuations of the concentration of radioactive substances, theoretical analysis should be performed on the both bases of hydraulic infiltration law and of adsorption theory.

Basing upon such a standpoint, Kaufman and others¹⁾ presented a theoretical rule governing the concentration of the substance dissolved in ground water. However, this theory should be applied only to a water flow in a certain saturated aquifer.

The dilution effect of ground-water and the behaviour of radioactive substances under a ground-water table are of great importance but the phenomena of adsorption occurring above the ground-water table, where the strata is usually unsaturated, should be noted as a more important fact which would take place in the process of radioactive contamination of ground-water. In this case, since the hydraulics of infiltration

is extremely complicated by such factors as capillary force, entrapped air pressure, distribution of particle size and others, its theoretical analysis has not been accomplished yet. Furthermore, the mechanism of adsorption is also very complicated because the physical or the chemical characteristics of soil particles have a plenty of variety, in addition, the waste solution usually contains various electrolytes, both cations and anions.

In this paper, in order to simplify the procedure of the analysis, only few significant factors are taken into account under an assumed ideal condition such that the waste liquid, containing only one dissolved substance, flows downwards one-dimensionally, through homogeneous, unsaturated porous soil media. Then, a basic consideration is given to formulate the local and the time-distributions of ionic concentration (or the intensity of radioactivity) in the flowing waste as well as the accumulation rate of such adsorbed substances in the media.

Thus, in Article 2, on the basis of Horton's Law²⁾ of infiltration and the theory of monomolecular adsorption by Langmuir³⁾, two fundamental differential equations are introduced, which were finally solved theoretically on the concentration of ion, being represented as a function of time and location.

Furthermore, this theory is checked with a result of experiments. The result shows, as stated in Article 3, that the time-concentration curves observed experimentally and obtained theoretically at the bottom of the model filter column agreed qualitatively well with each other. The laboratory experiment is carried out by feeding an inactive CoCl_2 solution on a filter layer, under a constant head, after verifying the adequacy of our theoretical premises by a similar experiment with distilled water.

The final objects of this study are, (A) to investigate the degree of soil contamination caused by rainouts following to a nuclear explosion and by an accidental release or a leakage of radioactive liquids at nuclear reactors or hot-laboratories, in connection with the site selection or the construction of such facilities, and (B) to obtain further informations and reference data for the underground disposal of radioactive liquid wastes. In view of the importance of these problems, it is really desired that any sort of study on them, either theoretical or experimental, will be more developed in the future.

2. Theoretical Consideration

Theories have been developed well by many researchers on the motion of liquid in saturated media. However, in unsaturated media, the flowing mechanism is complicated with the aforementioned reasons, generally being very difficult to be analysed and formulated. As far as we know, only Philip⁴⁾ proposed a theory after

developing the Darcy's Law. Furthermore, a few researchers, Horton²⁾ and Uchida⁵⁾, presented several experimental formulas on the rate of infiltration or the advancing velocity of wet front.

With respect to the mechanism of adsorption, on the other hand, classical adsorption equilibrium formula by Gibbs⁶⁾ and Freundlich⁷⁾ are very familiar with us. Also, Langmuir's Theory³⁾, being led under an assumption that the adsorption phenomena occur monomolecularly on contact layers of plane surface, where the energy of adsorption is kept constant at any part of it, and Brunauer and Others' Theory⁸⁾, based on a similar assumption, but on polymolecular contact layer, comes into notice.

Now, Horton's Formula of infiltration, being highly evaluated by its good accordance with various field data, and Langmuir's Theory of monomolecular adsorption, being easily handled theoretically without losing any correspondence to experimental results, are both accepted as the basic laws in our study on introducing a fundamental quantitative relationship.

Assuming that a solution which contains only one kind of ions infiltrating to the surface soil layer one-dimensionally, and taking a small portion of soil, to which depth from the soil surface is z , the changing rate of concentration of the adsorbable substance contained in the liquid can be quantitatively related to the rate of accumulation of the substance adsorbed in the soil portion, according to the law of conservation of mass.

$$\frac{\partial(C\theta)}{\partial t} + \frac{\partial(Cu\theta)}{\partial z} = -\frac{\partial q}{\partial t} \quad \dots\dots\dots(1)$$

where, C = concentration of the adsorbable substance contained in a unit volume of medium soil,

q = mass of the adsorbable substance stored in a unit volume of medium soil,

u = linear pore velocity of liquid flowing downwards through the soil layer,

$\theta = PS$,

P = porosity of the soil layer,

S = degree of saturation,

t = time,

z = depth measured from an origin at soil surface.

In this equation, θ and u are considered to be functions of z and t . However, θ can be regarded as relationless to z and t , because the porosity P is a constant, when the natural consolidation of soil is neglected, and the degree of saturation S is also invariable, since the storage effect of pore may be excluded excepting at the final stage of infiltration. Similarly neglecting the storage effect of pore, u is considered to depend only upon t , because the flow is only downward.

According to the assumption by Dupuit-Forchheimer⁹⁾, the infiltrating velocity v

of the flow per unit horizontal area is expressed by

$$v = \Phi u, \quad \dots\dots\dots(2)$$

then equation (1) can be written as

$$\Phi \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial z} = - \frac{\partial q}{\partial t}. \quad \dots\dots\dots(3)$$

The rate of adsorption may be expressed mathematically in the same manner as used in our former study¹⁰⁾. Thus, by means of symbols of φ and θ , respectively representing a total number of adsorption beds charged in a unit volume of soil and a number ratio of beds, where the adsorption has been completed, to the total number, the rate of positive adsorption is given by $p_1\varphi vC(1-\theta)$ while the rate of desorption by $p_2\varphi\theta$, where p_1 and p_2 are the coefficients for each of the two rates. Consequently an apparent rate of adsorption is expressed by

$$\frac{\partial q}{\partial t} = p_1\varphi vC(1-\theta) - p_2\varphi\theta. \quad \dots\dots\dots(4)$$

At an equilibrium state of adsorption, a quantitative relationship between p_1 and p_2 is determined, as $\partial q/\partial t$ in equation (4) naturally becomes zero. Expressing both of φ and θ as functions of q and the adsorption capacity of soil a , equation (4) can be rewritten as

$$\frac{\partial q}{\partial t} = kvC(a-q), \quad \dots\dots\dots(5)$$

where k is an adsorption rate coefficient.

Here, boundary conditions may be presented by equations (6), which mean that, at the soil surface where z is zero, C must be an original concentration C_0 of the adsorbable substance in the liquid, and that, at any depth of z , q should be zero so far as the wet front does not reach there.

$$\left. \begin{aligned} C(z = 0, t = t) &= C_0, \\ q(z = z, t = \frac{\Phi z}{v}) &= 0, \quad 0 \leq t \leq \frac{\Phi z}{v}, \end{aligned} \right\} \quad \dots\dots\dots(6)$$

where \bar{v} is a mean value of v from $t=0$ to $t=t$. Solving equations (3) and (5) under the conditions in equations (6), q and C will be obtained, both resulting in a functional form of z and t .

For simplifying the mathematical analysis, we substitute v for a total discharge of fluid per unit sectional area

$$V = \int_0^t v dt$$

and substitute z with l , which is a volume of soil prism having a length z and a unit sectional area. Then, we can rewrite operators as

$$\frac{\partial}{\partial t} = v \frac{\partial}{\partial V},$$

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial l},$$

and

$$\bar{v} = \frac{1}{t} \int_0^t v dt = \frac{V}{t}.$$

Accordingly, equations (3), (5) and (6) are reformed as follows;

$$\phi \frac{\partial C}{\partial V} + \frac{\partial C}{\partial l} = -\frac{\partial q}{\partial V}, \quad \dots\dots\dots(7)$$

$$\frac{\partial q}{\partial V} = kC(a-q), \quad \dots\dots\dots(8)$$

$$\left. \begin{array}{l} C(l=0, V=V)C_0, \\ q(l=l, V=\phi l) = 0, \quad 0 \leq V \leq \phi l. \end{array} \right\} \quad \dots\dots\dots(9)$$

Comparing the above three equations with the equations and the boundary conditions proposed in our former study¹⁰⁾ respectively, it is easily found that their forms coincide mutually if the following correspondence of notations is taken.

$$\begin{array}{lll} M-C, & S-q, & t-V, \\ Z-l, & S_e-a, & aK-k, \\ v-1. & & \end{array}$$

Therefore, referring the result in the former study, the required solution in this case is easily given by

$$\frac{C}{C_0} = \frac{\exp. \{C_0 k(V-\phi l)\}}{\exp. \{k a l\} - 1 + \exp. \{C_0 k(V-\phi l)\}}, \quad \dots\dots\dots(10)$$

$$\frac{q}{a} = \frac{\exp. \{C_0 k(V-\phi l)\} - 1}{\exp. \{k a l\} - 1 + \exp. \{C_0 k(V-\phi l)\}}. \quad \dots\dots\dots(11)$$

Applying Horton's Formula on infiltration, we obtain

$$v = v_c + (v_0 - v_c)e^{-\lambda t}, \quad \dots\dots\dots(12)$$

where, v_0 = initial infiltration velocity,
 v_c = final infiltration velocity,
 λ = a constant.

Therefore the total discharge V can be represented by

$$V = \int_0^t v dt = v_c t + \frac{v_0 - v_c}{\lambda} (1 - e^{-\lambda t}). \quad \dots\dots\dots(13)$$

Substituting equation (13) and $l = z$ for equations (10) and (11), finally we can find the following solutions,

$$\frac{C}{C_0} = \frac{\exp. \left[C_0 k \left\{ v_c t + \frac{v_0 - v_c}{\lambda} (1 - e^{-\lambda t}) - \phi z \right\} \right]}{\exp. \{k a z\} + \exp. \left[C_0 k \left\{ v_c t + \frac{v_0 - v_c}{\lambda} (1 - e^{-\lambda t}) - \phi z \right\} \right] - 1}, \quad \dots\dots\dots(14)$$

$$\frac{q}{a} = \frac{\exp. \left[C_0 k \left\{ v_c t + \frac{v_0 - v_c}{\lambda} (1 - e^{-\lambda t}) - \Phi z \right\} \right] - 1}{\exp. \{k a z\} + \exp. \left[C_0 k \left\{ v_c t + \frac{v_0 - v_c}{\lambda} (1 - e^{-\lambda t}) - \Phi z \right\} \right] - 1} \dots\dots\dots(15)$$

Equation (14) gives the ionic concentration *C* in the portion of liquid flowing downwards through the horizontal plane of depth *z*, at any time *t*. Here, the values of *C*₀, *k*, *v*₀, *v*_{*c*}, *λ* and *Φ* would be properly presumed, while the value of *a* may be estimated as follows, by the similar way as Kaufman and others⁽¹⁾.

Let an initial porosity is *Φ*₀, the time when the wet front of liquid reaches to the bottom of the column is *t*₀ and the time required to saturate the adsorbing beds contained in this column is *t*₁, then, by the law of continuity, the following equation is established,

$$\int_0^{t_1} v \, dt = (\Phi - \Phi_0)z + \int_{t_0}^{t_1} v \, dt \dots\dots\dots(16)$$

On the other hand, since the amount of in- or out-flowing adsorbable substance is *C*₀ ∫₀^{*t*₁} *v* *dt* or ∫_{*t*₀}^{*t*₁} *Cv* *dt* respectively, and the amount of adsorbed substance accumulated in the column becomes *C*₀*Φz* + *az*;

$$az + C_0 \Phi z + \int_{t_0}^{t_1} C v \, dt = C_0 \int_0^{t_1} v \, dt \dots\dots\dots(17)$$

Hence finally we obtain

$$a = \frac{1}{z} \left[\int_{t_0}^{t_1} (C_0 - C) v \, dt - C_0 \Phi_0 z \right] \dots\dots\dots(18)$$

In the previous analysis, the natural decay of the dissolved substance is not taken into account. When it is a radioactive nuclide, for instance, we must consider the basic decay formula

$$I = I_0 [-0.693t/T], \dots\dots\dots(19)$$

where, *I* = intensity of radioactivity in the solution,

T = half life of the nuclide.

On the other side, since the physical or the chemical characteristics of solution may be almost identical whether an electrolyte in it is radioactive or not, we can also solve the adsorption problem in such a case of radioactive liquid, in the light of the analytical process previously adopted. Thus, by substituting *C* for *I* and introducing equation (19) to the analytical process, equation (14) can be converted to a final solution

$$\frac{I}{I_0} = \frac{\exp. \left[I_0 k \left\{ v_c t + \frac{v_0 - v_c}{\lambda} (1 - e^{-\lambda t}) \right\} - \Phi z \right]}{\exp. \{k a z\} + \exp. \left[I_0 k \left\{ v_c t + \frac{v_0 - v_c}{\lambda} (1 - e^{-\lambda t}) \right\} - \Phi z \right] - 1} \cdot \exp. \{-0.693t/T\} \dots\dots\dots(20)$$

3. Experimental Studies

Experiments were performed in our laboratory in order to examine the adequacy of our theory introduced in the preceding article.

A. Preliminary test with distilled water.

The purpose of the preliminary test was to ascertain the validity of our hydraulic assumptions used in the above, being that Horton's Law is applicable to the infiltration in the model filter layer and that the porosity and the degree of saturation are regarded as invariable, without any bearing on location and time.

Experimental apparatus used in this test is shown on Fig. 1-a. Under a constant head, distilled water was supplied continuously to the upper part of the filter column and, in order to know the filtration velocity, the amount of filtrated water flowed out from the bottom of the column, for one minute, was measured intermittently once a minute. Moreover, as shown in Fig. 1-b, the local and the time changes of electric conductivity were measured by means of platinum electrodes, which were inserted to the sand layer. Then, the time change of the degree of saturation in the filter sand was estimated by comparing the values of conductivity, thus measured, with a calibration curve, which had been previously prepared by an experiment with the same apparatus, but under several known degrees of saturation. The platinum electrodes were located at 21.5 cm for No. 1, at 73.5 cm for No. 2 and at 121.5 cm for No. 3, all below the sand surface.

The filter column was filled with slow filter sand being used at Matsugasaki Water Purification Plant, Kyoto City, of which specific weight was 2.60, effective size was 0.36 mm and uniformity coefficient was 1.81. After washing it with 0.1 N hydrochloric acid, it was filled into the column, with a depth of 156 cm. Its porosity was 48.4% and its moisture was 12.3%. The infiltration experiments were carried out under a steady condition of water column of 9 cm deep above the sand surface.

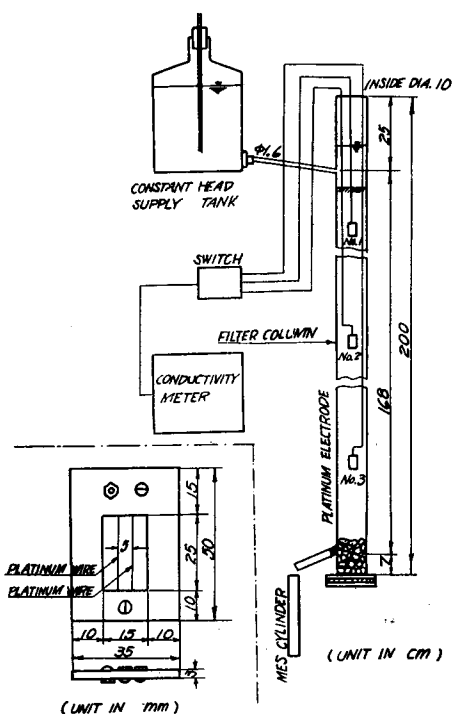


Fig. 1-b.
Platinum
Electrode

Fig. 1-a.
Experimental
Apparatus

The time changes on the degree of saturation and on the filtration velocity were shown in Fig. 2 and Fig. 3, respectively. The time fluctuation of the amount of filtrated water was also shown in Fig. 3. As shown on Fig. 2, since air bubbles were sealed in the layer by the entrapping air pressure in the pores, the degree of saturation was as low as 30-50% when a steady state came, then it remained almost constant. The peak of the degree of moisture appeared for a short period, within around 15 minutes after the time starting the filtration. Such phenomena are probably due to that the soluble substances, which had adhered originally to the sand grains, were inevitably eluted by the wet front. Also a slight local variation of the degree of moisture was observed, but it was considered to be within a tolerance range of errors on measurement.

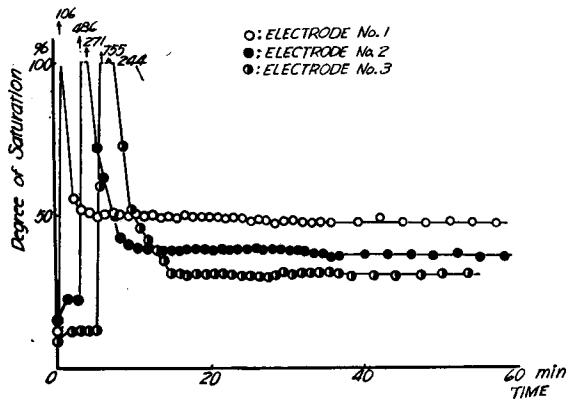


Fig. 2. Observed Variation of Degree of Saturation

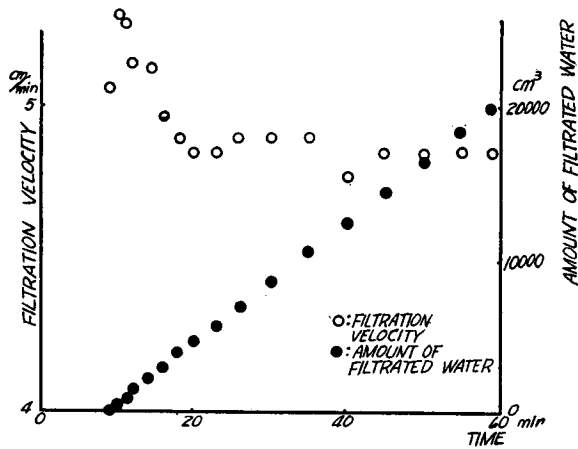


Fig. 3. Filtration Velocity and Amount of Filtrated water

Since not any visible shrinkage was observed, and hence the porosity seemed constant everywhere in the filter column during a filter run, our assumption taking a constant value of θ regardless of z and t would be adequate.

The observed value of filtration velocity fluctuated somewhat randomly, as shown on Fig. 3, but Horton's Law would be applicable even to such a data, by taking into account its general tendency.

B. Infiltration test with CoCl_2 solution.

Two runs of infiltration tests were carried out with CoCl_2 solution, in order to ascertain the adaptability of our theory. A series of data obtained by observing the time

fluctuation of ionic concentration of Co^{++} in the filtrate was compared with the theoretical results computed by equation (14).

As a dissolved ion to be dosed, Sr^{++} , one of its isotopes is ^{90}Sr , having a long life and significant biological effects, would be preferable. However, the quantitative analysis of Sr^{++} is rather difficult when Ca^{++} or Mg^{++} ion coexists with it, especially in such a case that tap water is used as a solvent. This is why we used Co^{++} instead of Sr^{++} .

By using the same apparatus and the same procedure as in the preliminary test, the ionic concentration of Co^{++} in the filtrate was colorimetrically determined with 0.5% solution of Nitroso-R salt after converting the recorded amount of filtrate to the filtration velocity.

The conditions in each run were as follows :

(a) Run No. 1

| | |
|-------------------------------------------|--------------------------------------------------------------------|
| Kind of medium | = Slow filter sand at Matsugasaki Water Purification Plant, Kyoto. |
| Depth of the filter layer | = 158 cm |
| Porosity | = 42.9% |
| Water depth above the surface of layer | = 8.5 cm |
| Moisture content before starting run | = 3.21% |
| Initial concentration of Co^{++} | = 148 ppm |

(b) Run No. 2

| | |
|-------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Kind of medium | = Surface soil collected near by the building of Sanitary Engineering Department, Kyoto Univ. (specific weight was 2.59, effective size was 0.26 mm and uniformity coefficient was 6.93). |
| Depth of the filter layer | = 68 cm |
| Porosity | = 40.8% |
| Water depth above the surface of layer | = 111 cm |
| Moisture content before starting the run | = 46.6% |
| Initial concentration of Co^{++} | = 1,015 ppm |

Time fluctuations of the filtration velocity and of the amount of filtrate on Run No. 1 or Run No. 2 were shown in Fig. 4 or Fig. 5, respectively. The observed data on Run No. 1 satisfies Horton's Law fairly well, while on Run No. 2, not so good. This is probably due to, other than a slight fluctuation of the water depth above the filter surface, mainly the clogging at the lower part of the filter layer with fine sand and silt, which passed the pores then precipitated on the filter bottom. However, since its influence would not be so serious, our assumption that θ is constant might be acceptable.

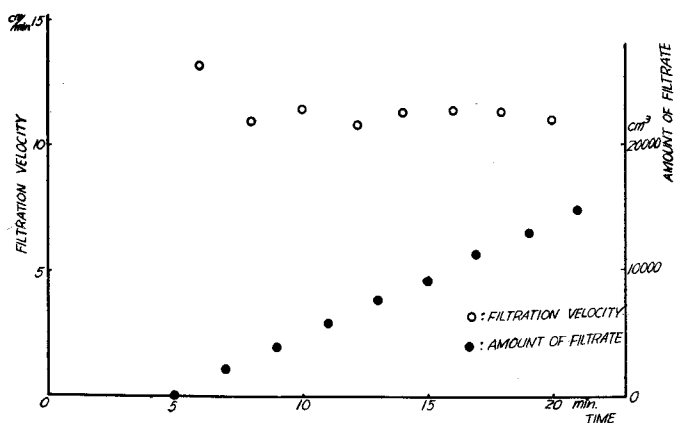


Fig. 4. Filtration Velocity and Amount of Filtrate (Run No. 1)

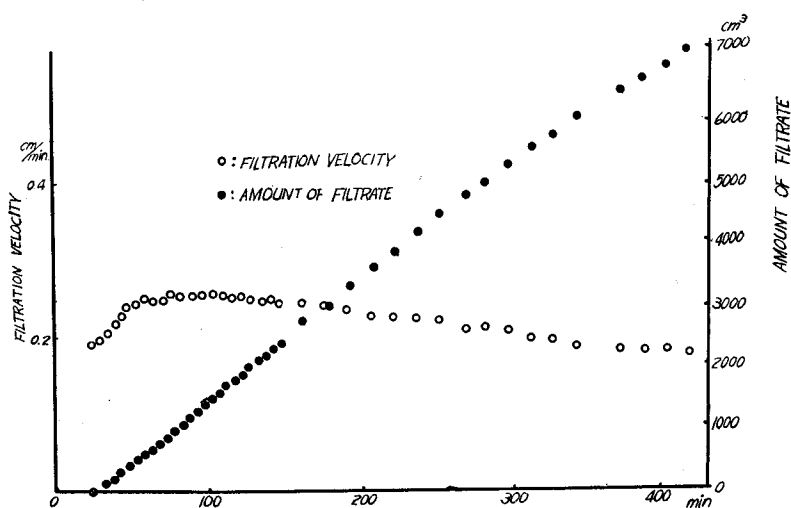


Fig. 5. Filtration Velocity and Amount of Filtrate (Run No. 2)

The time-concentration curve on Run No. 1 or Run No. 2 would be obtained by fitting a curve to the observed data, marked with the empty circles in Fig. 6 or Fig. 7. In order to compare it with our theory, a group of theoretical curves, corresponding to various k values, was drawn on each of these two figures by full lines.

As shown in Fig. 6 and Fig. 7, the tendencies of experimental and theoretical results well coincide with each other, qualitatively, both in S-shape. Quantitatively, however, their mutual correspondence remained uncertain because we were unable to determine a value of k for a given condition. According to Langmuir's Theory³⁾, which assumes that the adsorption occurs only on the first monomolecular layer of plain surface, where the energy of adsorption is kept constant, the value of k should

- a. In general, Horton's Infiltration Formula is applicable to such phenomena.
- b. Degree of saturation and porosity may be regarded as constant, unconcerned with time and location.
- c. The result of the authors' theoretical analysis, equation (14) (or (20)), was verified to be qualitatively correct by model experiments. However, on the value of the constant k , which controls adsorption behaviour, our study was still incomplete. It is necessary to develop a further study on it.

The abovementioned is a basic study in an ideal case. In a natural case, however, the phenomena are much complicated, being affected by local soil conditions such as entrapped air pressure, capillary force, soil formation, characteristics of soil and so on. Moreover, in a field problem, it is noted that the effect due to any specific property of the infiltrating liquid such as the mutual interference between coexisting electrolytes contained in it, for example, must be carefully considered.

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