

PHOSPHATE TRANSPORT IN ILLITE DUE TO CONSOLIDATION

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Abstract—The conditions were studied under which consolidation loading caused the release of phosphate from a saturated illite clay. P^{32} tracer techniques were employed to follow the movement of phosphate in composite samples composed of tagged and untagged portions. The samples, initially consolidated to 1.0 kg cm^{-2} stress were reconsolidated to 0.1, 0.5, 2, 4 and 8 kg cm^{-2} stress and the transport of phosphate was monitored by counting the radioactivity of 0.01-in. thick sections sliced parallel to the major principal plane. Corrections were applied for P^{32} - P^{31} self-diffusion. It was found that: (1) for low phosphate concentrations there was no observable transport due to consolidation type flow; (2) for high phosphate concentrations and for stresses less than or equal to the preconsolidation load there was no observable transport due to consolidation type flow; and (3) for high phosphate concentrations and for loads above the preconsolidation load there was detectable transport of phosphate, presumably due to the consolidation flow. A mechanism based on self-diffusion plus uniform flow was able to semi-quantitatively explain the test results.

INTRODUCTION

Problems of ion transport in clays have become increasingly significant with the increase in concern over pollution problems. In particular, the permanency with which contaminating ions are retained in clays must be studied to determine whether such clays act as permanent sinks for pollutants or whether the polluting ions can be released from clays into an environment where they may have harmful effects. The results reported in this paper are a part of a comprehensive study to determine the effects of engineering operations on the possible release of phosphates from sediments into overlying waters. This paper experimentally delineates the conditions under which one dimensional consolidation loading causes transport of phosphates in an illite clay.

The simultaneous flow of water and ions in clay systems has been treated theoretically by numerous investigators including Abd-El-Aziz (1964) and Olsen (1969). The theoretical treatment of the interaction of ions with clays during simultaneous transport has been developed by Lindstrom and Boersma (1970). The analysis of ion transport due to ground water flow has been presented by Cearlock (1972). Finally, the analysis for ion flow induced by consolidation loading has been given by Greenberg and Mitchell (1971).

While experiments have been performed to study the diffusion of ions under chemical gradients in clays, no experiments have yet been published to demonstrate the simultaneous transport of ions and water under hydrodynamic loading. The experiments described herein were designed to determine semi-quantitatively the conditions under which the phosphate anion is transported as a result of consolidation loading in an illite clay.

EXPERIMENTAL

Hydrodynamic pressure gradients were induced by using the one-dimensional consolidation test, shown in Fig. 1a. When a load is applied to a completely saturated consolidation sample, the stress initially causes the pressure in the pore water to increase because the water is much less compressible than the soil skeletal structure (Leonards, 1962). This initial pore water pressure distribution is shown in Fig. 1(b).

If the load on a layer of highly compressible porous saturated soil (such as clay) is increased, the layer will compress as the excess water drains out of the soil. This process is termed consolidation. The added load or pressure per unit of area that produces consolidation is known as the consolidation pressure or consolidation stress. In the process, the excess water pressure

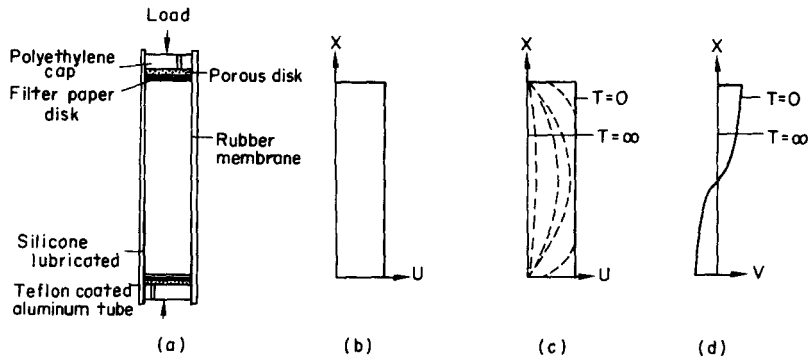


Fig. 1. Consolidation test conditions, (a) apparatus, (b) initial excess pore pressure distribution, (c) time-dependent pore pressure dissipation and (d) time-dependent water flow velocity.

decreases and the effective stress (stress carried by soil skeleton) increases. After a long (theoretically infinite) time the excess hydrostatic pressure becomes equal to zero and the total consolidation pressure becomes equal to the effective stress. It is assumed that flow of water is vertical only, that drainage is from upper and lower surfaces of the sample, and that the consolidation stress is uniform throughout the sample.

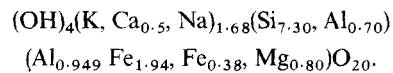
The time dependency of distribution of effective stress in the soil is shown in Fig. 1(c). The reduction in pore water pressure is not only time dependent but is also a function of position along the cylinder. This dependency is because resistance to flow of water in soils arises throughout the mass due to the small size and tortuosity of the flow path.

Because the ends of the sample are at atmospheric pressure, the water will begin to flow out to both ends in a time-dependent manner. Water moving through the pores in the soil mass will drag ions with it. Therefore, the hydraulic gradient causes the gradual movement of the ions of the soil. The velocity of the pore water depends on position and time in the manner shown in Fig. 1(d). Minimum pore water pressure occurs at the two ends of sample, and the maximum velocity will be at these points. Similarly, the minimum velocity (zero) will be at the center of the sample. Because electrostatic and electrodynamic forces tend to hold the ions to the soil particles, hydrodynamic flow of the ions will occur at a velocity equal to or less than the velocity of the water.

The experimental program was designed to study phosphate ion transport as a function of hydraulic pressure gradient and of overall ion concentration in the pore fluid. Because it was desired to measure transport of phosphorus under hydrodynamic pressure gradients, transport due to the other process was minimized. In particular, diffusion due to chemical concentration gradients was eliminated. To accomplish

this, the P concentration throughout the sample was held constant. Nevertheless, self diffusion, defined as interdiffusion of identical ions under no chemical gradient, introduced an artifact into the data for which a correction was applied.

The soil used in this investigation was Grundite Bond Clay from A. P. Green Refractory Products in Joliet, Ill. Grundite contains a high percentage of illite, a clay mineral having a generalized formula:



The material is uniform with an average grain dia. of approximately $2 \mu\text{m}$. Solid particles are plate shaped and the ratio of dia. to thickness is about 10:1.

Potassium dihydrogen phosphate (KH_2PO_4) dissolved in water was used as the phosphate solution, since most investigators have concluded that the ionic form of phosphate in the soil would be H_2PO_4^- . P^{32} carried in hydrochloric acid as KH_2PO_4 was dispersed in the solution for tagged samples. A quantity of P^{32} having an initial activity of 1 mCi ml^{-1} and $51 \text{ Ci mg}^{-1} \text{ P}$ was obtained from Amersham-Searle for use in this investigation.

The variables examined in the experimental program were:

(1) Effects of magnitude of pore pressure gradient on P transport; and,

(2) Effect of overall P concentration on the P transport. The test program consisted of consolidating several series of samples using stresses of 0, 0.1, 0.5, 2, 4 and 8 kg cm^{-2} . The 0 kg cm^{-2} tests were performed to estimate the correction for self-diffusion. In these tests, essentially zero loading was maintained for different lengths of time and for the various P concentration used. The tests determined the variation in self-diffusion coefficient as a function of P concentration.

Within each series, the phosphate content was held

constant. Series were prepared using phosphate concentration of 0.005, 0.2, 1 and 2 mg P g⁻¹ dry soil.

In order to form the material from which individual samples were made, three master samples, one tagged with P³² and the other two untagged, were prepared for each phosphate concentration. The untagged samples contained KH₂PO₄ soln; the tagged samples KH₂PO₄ soln with a trace amount of P³². These samples were consolidated from slurry to 1 kg cm⁻². The proper amount of water in the slurry was that required to give a consistency sufficiently fluid to allow the air bubbles to be expelled by gentle vibration. The actual amount of added solution was 406 ml H₂O per 400 g dry soil. The different concentrations of KH₂PO₄ solution were obtained by diluting a stock solution which contained 17.30 g KH₂PO₄ in 2 l. water. In order to avoid concentration differences in the samples, the amounts of total added phosphorus for the untagged and tagged samples were exactly equal.

The slurry was placed in a Teflon-coated tube 10.75 in. long, with a 2 in. o.d. and a 1.75 in. i.d. The inside surface of the consolidation tube was lightly lubricated with Dow Corning Silicone Oil. A rubber membrane was vacuum expanded within the tube (see Fig. 1a). In the master samples, for each concentration three tubes were used; one for tagged slurry and two for untagged slurry. A polyethylene loading cap, a porous plastic disk and a filter paper disk were introduced before filling the tube with slurry. After sufficient slurry was introduced into a tube, a filter paper, a porous plastic disk and a polyethylene cap were also placed at the top. The polyethylene caps were perforated to permit expulsion of water. The porous disks were deaired by boiling.

The master samples were then consolidated one-dimensionally through a loading yoke, drainage being allowed at both ends. The loading increments used gave consolidation stresses equal to 0.0625, 0.125, 0.25, 0.5 and 1 kg cm⁻². Each load was allowed to stand until compression had effectively ceased before the subsequent load was applied. For each increment, a curve of compression vs time was obtained. Homogeneity and uniformity of the samples were considered in determining the increment of loading. Small load increments give uniform samples because the soil particles shift their position gradually and the skeleton of soil compacts uniformly. With this procedure it was possible to obtain almost identical particle orientation distributions throughout the sample.

According to Rowell *et al.* (1967) 1 month is required for equilibrium of P³²-P³¹ in soils. Consolidation to 1 kg cm⁻² required 1 month; therefore it is assumed that the P³² was equilibrated in the tagged samples during the consolidation. After consolidation, the mas-

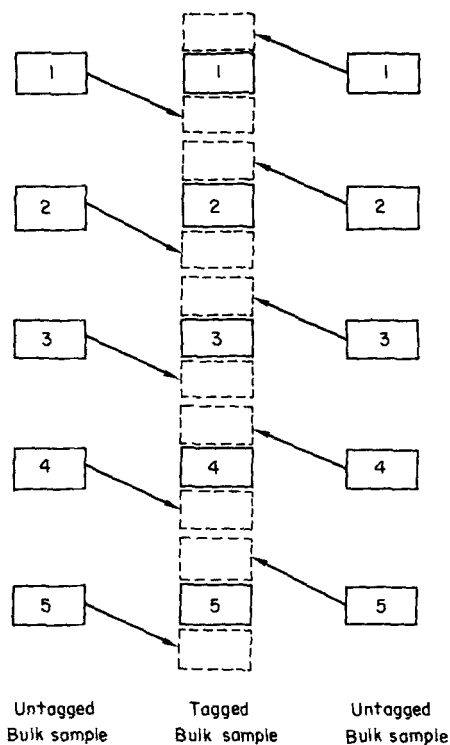


Fig. 2. Assembly of individual test samples from master samples.

ter samples were extruded from the tubes and sectioned into 0.750 in. pieces as shown in Fig. 2.

For the final test series, Teflon coated tubes 2.875 in. long, with a 2 in. o.d. and a 1.75 in. i.d. were used to contain a tagged section sandwiched between two untagged sections. The tubes were assembled by first introducing a polyethylene loading cap, a porous plastic disk and a filter paper; followed by a 0.75 in. untagged section, a 0.75 in. tagged section and a 0.75 in. untagged section of the master samples; and finally, by a filter paper, porous plastic disk and polyethylene loading cap.

The five samples so prepared were one dimensionally consolidated with drainage from both ends. During consolidation the samples were kept wet to prevent water loss due to evaporation. The final stresses employed were 0, 0.1, 0.5, 2.4 and 8 kg cm⁻², and the desired stress was applied in a single increment. Deflection vs time was monitored during loading. A total of 25 individual samples was tested.

After consolidation ceased, the samples were carefully extruded from the tube and sectioned into pieces 0.01 in. thick. From each sample 180-200 sections were obtained. Sections were placed in aluminum foil and oven dried for 24 hr. Each section was individually

ground to pass a 200 mesh sieve and was placed in a preweighed planchet. Approximately 0.500 g of powder was smoothed and compacted in the planchet with the aid of a fitted plunger. The planchet and powder were then weighed to 0.1 mg accuracy.

Radioactivity assay was done using a Nuclear-Chicago model 8703 gas flow counting system. The number of counts is proportional to the counting time and is also a linear function of the weight of the sample. In this investigation, a 10 min counting time was used for an approximately 500 mg dry sample, the weight of a 0.01 in. section. The average of two countings was taken for each individual section. In order to normalize the values, the results were expressed in counts $\text{min}^{-1} \text{g}^{-1}$ dry soil. Each sample had been divided into about 200 sections. The average of the counts from the first 10 and the last 10 sections was taken as background in each sample.

Data available are the weights of the sections, and the time and counts given as a printed output by the Nuclear-Chicago equipment. These numbers were punched on cards for computer analysis. Some 8000 data points were so accumulated.

ANALYSIS OF TEST RESULTS

In order to assess the amount of hydrodynamic transport, the effect of self diffusion must be removed. By eliminating both chemical and hydrodynamic diffusion, the distribution of the radioactive species was used to determine the self diffusivity of phosphate. The P^{32} distribution curves for tests performed at various consolidation pressures and ion concentration are shown in Fig. 3. For all samples counts have been normalized to a constant value at the midpoints and distance has been normalized to a constant sample length. The dots represent data points for total transport after consolidation. The solid lines represent the contribution due to self diffusion determined from the experimental tests in which essentially zero loading was maintained.

In sandwiching the tagged section between the untagged sections, water and soil particles were initially at a single interface and the P^{32} was distributed uniformly. In the process of consolidation, water and soil particles do not stay in their initial position. When a load is applied to the sample, the soil particles compress inward and the liquid drains outward. The amount of movement depends on the applied load. Drainage of water causes a change in the void ratio (ratio of volume of voids to the volume of solids) of the sample. For a given sample under consolidation pressure, the distance moved by the water and the distance moved by the soil particles from the initial interface

can be evaluated from the initial and final void ratios.

In Fig. 4, L , LW and LS denote the initial length of tagged sample, the final length over which initially tagged water is distributed, and the final length over which the initially tagged soil is distributed, respectively.

LS and LW are obtained:

$$LW = L \frac{1 + 1/e_f}{1 + 1/e_i} \quad LS = L \frac{1 + e_f}{1 + e_i}$$

where e_i = void ratio before loading

e_f = void ratio after loading.

The values of L , LW and LS are shown in Fig. 3.

DISCUSSION OF TEST RESULTS

The effect of non-self-diffusion-dependent transport of P can be evaluated by reference to Fig. 3. The solid curves represent the predicted distribution of P^{32} due only to self-diffusivity and the dots represent the actual distribution of P^{32} in the samples after consolidation. Thus, data points lying outside the self-diffusion curve suggest some additional transport mechanism. The assumption in designing this experimental series was that such additional transport would be due to water flowing out of the sample.

Reference to Fig. 3 shows that transport in excess of that attributable to self-diffusivity clearly occurred at 2 mg P g^{-1} dry soil for consolidation stresses of 2, 4 and 8 kg cm^{-2} . In addition, there is evidence of additional transport for 0.2 mg P g^{-1} dry soil for 4 kg cm^{-2} loading. However, this latter result is viewed with some doubt because that sample was loaded eccentrically and some soil was lost from the tube in the consolidation process. In all other cases, while some non-self-diffusion dependent transport may have occurred, the resolution obtainable from the experimental technique employed was not sufficient for its detection.

To explain the non-self-diffusion part of the ion transport, it is useful to compare the actual data points with the final length over which the initially tagged water was distributed after consolidation. This length is denoted by LW on Fig. 3. The simplest hydrodynamic flow model would suppose that the radioactive P would extend outward only as far as LW (or the outer limit of self diffusion if that exceeds LW). Depending on the location of the distribution curve with respect to LW , the three mechanisms shown in Fig. 5 may be postulated:

1. The amount of transported water is larger than the amount of transport of ions shown by the distribution curve; i.e. the ions are not being transported with

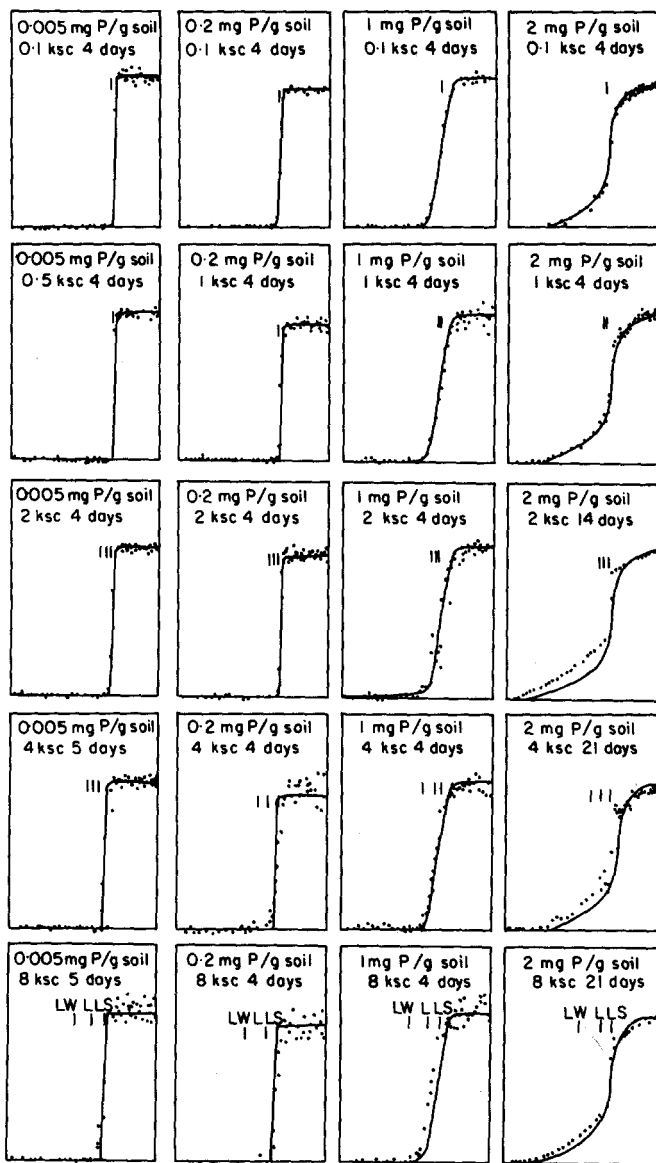


Fig. 3. Total transport data with self diffusion superimposed plotted as normalized counts $\text{min}^{-1} \text{g}^{-1}$ vs normalized distance.

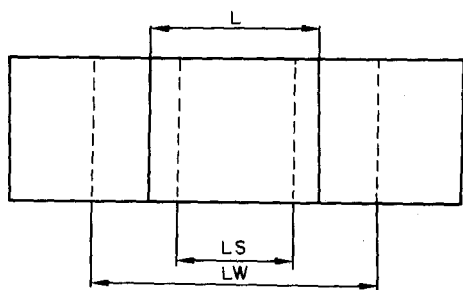


Fig. 4. Initial tagged-untagged interface (L), and limits of tagged water (LW) and tagged soil (LS) after consolidation.

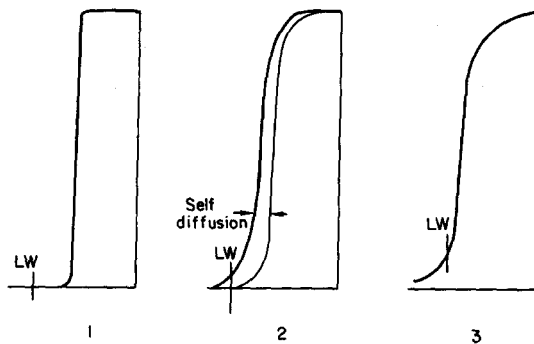


Fig. 5. Idealized modes of ion transport test results.

the water. This mode was observed at low P concentration (0.005, 0.2, 1 mg P g⁻¹ dry soil). At this low concentration of phosphate, essentially all of the added ions are probably sorbed onto the clay particles and would not be affected by the flow of water.

2. The distribution curve terminates exactly at $LW +$ the self diffusion distance. This possibility can be interpreted as strong evidence for transport of ions by the water alone. Ions move with the water flow; therefore, the ion-transport depends simply on the flow. This case was observed at higher phosphate concentration and for high consolidation stresses (2 mg P g⁻¹ dry soil and 2, 4 and 8 kg cm⁻²). This phenomenon could be explained by a combined mechanism. A part of the transport would be due to flow carrying ions to LW . The transport beyond LW would be accounted for by self-diffusion of phosphate ions in the water. This self-diffusion would result in tagged phosphate diffusing out into initially untagged water. On a semi-quantitative basis, this mechanism appears promising for explaining the experimental observations. The validity of this mechanism is further supported by the observation that for consolidation stresses below the preconsolidation stress (1 kg cm⁻²), where there was little or no additional compression upon reconsolidating the samples (2 mg P g⁻¹ dry soil, 0.1 and 1 kg cm⁻²), self diffusion alone was capable of explaining all of the observed transport.

3. Transport of ions extends beyond $LW +$ self diffusion. This case was not observed in these studies.

In summary, for low concentration of added phosphate and for low consolidation stresses, all phosphate transport could be accounted for by self diffusion alone. At high concentration of added phosphate and for high consolidation stresses, phosphate transport could not be explained by either self diffusion or transport with a uniformly advancing water interface alone, but could be semi-quantitatively accounted for by a mechanism involving a combination of these two factors.

CONCLUSIONS

1. Self diffusion alone appears to explain the total transport for low P concentration (0.005, 0.2 mg P g⁻¹ dry soil) (see Fig. 3).

2. Self diffusion alone appears to explain the total transport for all concentrations at stresses less than or equal to the preconsolidation stress of 1 kg cm⁻² (2 mg P g⁻¹ dry soil, 0.1 and 1 kg cm⁻²).

3. For low concentrations and low consolidation stresses the experimental techniques were not sensitive enough to permit definite conclusions; however, self-diffusion alone appeared to explain the results. The apparent lack of transport due to flowing water may have resulted from the ions being sorbed onto the clay particles.

4. Self-diffusion alone cannot explain the total transport for high concentrations (2 mg P g⁻¹ dry soil) and high stresses (2, 4, 8 kg cm⁻²).

(a) A simple mechanism based on uniform flow of water in all pores is not satisfactory for explaining the excess transport for these concentrations and stresses. Radioactive phosphate extends beyond the tagged-untagged water interface for these cases.

(b) A conceptual model based on combination of flow transport and self-diffusion semi-quantitatively explains these data.

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Résumé—On a étudié les conditions dans lesquelles une charge de consolidation entraîne une libération de phosphate à partir d'une illite saturée. Des techniques utilisant P³² comme traceur ont été employées pour suivre le mouvement du phosphate dans des échantillons composites faits de parties marquées et non marquées. Les échantillons consolidés initialement sous une charge de 1.0 kg/cm² ont été reconsolidés

sous des charges de 0,1, 0,5, 2, 4 et 8 kg/cm² et le transport du phosphate a été suivi en comptant la radioactivité de tranches de 0,01 pouce d'épaisseur coupées parallèlement au plan principal le plus important. On a apporté les corrections pour l'autodiffusion P³²-P³¹. Les résultats suivants ont été obtenus: (1) pour les faibles concentrations en phosphate il n'y a pas de transport observable dû à un flux du type consolidation; (2) pour les fortes concentrations en phosphate et pour des charges inférieures ou égales à la charge de préconsolidation il n'y a pas de transport observable dû à un flux du type consolidation; (3) pour les fortes concentrations en phosphate et pour des charges supérieures à la charge de préconsolidation, il y a un transport de phosphate observable, probablement dû au flux de consolidation. Un mécanisme fondé sur l'autodiffusion plus un flux uniforme peut expliquer semi-quantitativement les résultats de l'essai.

Kurzreferat—Die Bedingungen wurden untersucht, unter denen Verfestigungsdruck die Freisetzung von Phosphat aus einem gesättigten Illiton hervorruft. Markierungsmethoden mit P³² wurden angewandt, um die Bewegung des Phosphates in Proben zu verfolgen, die sich aus markierten und nichtmarkierten Anteilen zusammensetzten. Die ursprünglich unter einem Druck von 1,0 kg/cm² verfestigten Proben wurden unter Drucken von 0,1, 0,5, 2, 4 und 8 kg/cm² wieder verfestigt und der Phosphattransport durch Messung der Radioaktivität in 0,25 mm dicken Schnitten verfolgt, die parallel zur größeren Hauptebene angelegt wurden. Korrekturen für die P³²-P³¹-Selbstdiffusion wurden vorgenommen. Es wurde gefunden, daß erstens bei niedrigen Phosphatkonzentrationen kein nachweisbarer Transport durch einen verfestigungsbedingten Fluß auftrat, daß zweitens bei hohen Phosphatkonzentrationen und bei Drucken, die niedriger als der oder gleich dem Verfestigungsdruck waren, kein Transport durch verfestigungsbedingten Fluß zu beobachten war, und daß drittens bei hohen Phosphatkonzentrationen und bei Drucken über dem Verfestigungsdruck ein nachweisbarer Phosphattransport wahrscheinlich als Folge eines verfestigungsbedingten Flusses auftrat. Ein Mechanismus, der auf Selbstdiffusion in Verbindung mit einformigem Fluß beruht, konnte die Versuchsergebnisse halbquantitativ erklären.

Резюме — Изучали условия при которых нагрузка консолидирования вела к освобождению фосфата из насыщенной иллитовой глины. Метод меченых атомов P³² использовался для прослеживания перемещения фосфата в сложных образцах, состоящих из маркированных и не маркированных порций. Образцы первоначально консолидированные до 1,0 кг/см² напряжения были вновь консолидированы до 0,1–0,5; 2; 4 и 8 кг/см². Транспортировку фосфата контролировали путем подсчета радиоактивности шлифов толщиной 0,01 дюйма, срезанных параллельно к главной плоскости. Ввели поправки на самодиффузию для P³²-P³¹. Нашли, что (1) при низкой концентрации фосфата не было заметной транспортировки в результате потока консолидирования; (2) при высокой концентрации фосфата и при напряжении ниже или равном нагрузке перед консолидированием также не было заметной транспортировки благодаря потоку консолидирования; и (3) при высоких концентрациях фосфата и нагрузках выше, чем перед консолидированием замечалось транспортирование фосфата, очевидно, вследствие потока консолидирования. Результаты исследования можно полукачественно объяснить механизмом, базированном на самодиффузии плюс однородный поток.