Effect of exchangeable sodium levels on physical properties of coal overburden samples having differing clay mineralogy
by Richard Henry Opper

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Soils
Montana State University
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Abstract:
The effect of different levels of exchangeable Na+ on the physical properties of overburden samples from eastern Montana and western North Dakota was studied. Samples having clay fractions dominated by either smectite, illite, or kaolinite were used in this research. The physical tests of hydraulic conductivity (K), coefficient of linear extensibility (COLE), shrinkage of briquets, and modulus of rupture (MOR) were used to indicate changes in physical properties.

The hydraulic conductivity of the smectite samples was essentially reduced to 0 at sodium adsorption ratio (SAR) values of 15, whereas all of the illite and kaolinite samples retained the ability to transmit water at SAR 15. Sample shrinkage reached a peak at SAR values of 10 for both the smectite and kaolinite sample groups with the kaolinite sample group showing the highest degree of swelling. No relationship between exchangeable Na+ levels and MOR values was observed for the illite or kaolinite sample groups though the MOR values for the smectite samples appeared to increase with increasing SAR values.

Some refinements to the concept of a critical ESP value of 15 for determining sodic soil conditions are offered as are areas of related research.

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COAL OVERBURDEN SAMPLES HAVING DIFFERING CLAY MINERALOGY

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RICHARD HENRY OPPER

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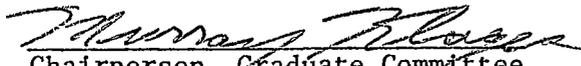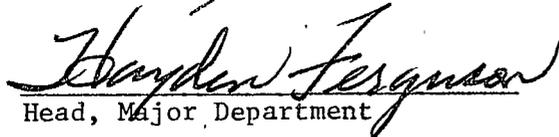
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Approved:

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ABSTRACT

The effect of different levels of exchangeable Na^+ on the physical properties of overburden samples from eastern Montana and western North Dakota was studied. Samples having clay fractions dominated by either smectite, illite, or kaolinite were used in this research. The physical tests of hydraulic conductivity (K), coefficient of linear extensibility (COLE), shrinkage of briquets, and modulus of rupture (MOR) were used to indicate changes in physical properties.

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Some refinements to the concept of a critical ESP value of 15 for determining sodic soil conditions are offered as are areas of related research.

INTRODUCTION

Soil physical problems, such as swelling, slow permeability, and crusting are major impediments to successful reclamation in the northern Great Plains where efficient use of available water is essential. The effect of adverse soil physical properties must be minimized in order to establish and maintain a vegetative cover on previously mined land. Exchangeable sodium is responsible for many of the physical problems exhibited in natural soil systems and in spoil material. This study is concerned with the effect of exchangeable sodium on the physical properties of overburden samples from proposed mine sites in the northern Great Plains.

Overburden samples with clay fractions dominated by three different mineralogical groups were used in this research. The illite samples were taken from the Tanner Creek area on the Crow Indian Reservation, Section 24, T9S, R38E. The kaolinite samples and all the smectite samples except Kiewit A and No. 531 were drilled in the Colstrip Area, Western Energy mine area B, Section 21, T9S, R40E. Sample 531 was taken from the vicinity of Underwood, North Dakota and location information for the Kiewit sample was unavailable.

The United States Department of Agriculture Handbook 60 (U. S. Salinity Laboratory Staff 1954) defines sodic soils as having exchangeable sodium percentage values of 15 or greater. The degree to which exchangeable sodium affects soil physical properties depends to some extent upon the clay mineralogy of the soil samples. Perhaps

a single exchangeable sodium percentage is an insufficient means of identification of potential sodium hazards in overburden samples of the northern Great Plains which are characterized by diverse mineralogical composition. While not designed as a reclamation study, this report should clarify the nature of sodium problems in soils and may refine the definition of and identification of potential sodium hazards.

REVIEW OF LITERATURE

A qualitative definition of swelling in clay-water systems might be that swelling is the adsorption of water by clay colloids which results in an increase in the volume of the colloidal system (Baver et al. 1972). The water initially entering a clay-colloid system tends to be structured around the colloidal surfaces in an oriented arrangement (Baver et al. 1972). Subsequent water either fills existing pore spaces within the system or enlarges those pores through swelling. The degree of swelling of a material is controlled by many factors including the amount and size of pores, the type and amount of cations and aluminum oxides, the degree of structure of the soil material, and the stability of aggregates (Davidson and Page 1956, Fathi et al. 1971). Swelling has a direct effect on the physical properties of soils, including the hydraulic conductivity, modulus of rupture, and the linear extensibility (Quirk and Schofield 1955, Richards 1953, Franzmeier and Ross 1968). Both the AASHO and the Unified engineering capability soil classification system are based in part on the potential shrinkage of soils (USDA 1971). An understanding of the dynamics of clay-water interaction clarifies the physical process of swelling.

Adsorption of Water by Clays

Hardy (1923) theorized that water in a clay-water system exists in two forms, one of which is crystalline and "ice-like." He suggested swelling in clays and soils is due solely to the adsorption

of vesicular (crystalline) water. Lauritzen and Stewart (1941) determined that the amount of shrinkage of a soil material depended upon the moisture range over which a given volume loss occurred. They concluded that shrinkage accompanying drying is dependent upon the manner in which the moisture is associated with the soil material and with the pore spaces within the soil mass. Low (1960) concluded that water exists in a structured form at the surface of soil clays, and that this structure imparts a high viscosity to adsorbed water. In later papers he elaborated on the adsorption of water by soil clays. Polar water molecules are attracted to the oxygen of clay surfaces by hydrogen bonds. Because of the directional nature of such bonds, water molecules in the second water layer can be expected to form somewhat weaker hydrogen bonds with the water molecules adjacent to the surface. A repeating sequence of water layers, each reproducing in part the structure of the tetrahedral oxygen sheet of the clay surface, is thus adsorbed on the surface of clay minerals. It is this structured water to which Low attributed the swelling of the system with the degree of swelling being determined by the thickness of the structured water layer (Low 1961).

Effect of Cation Amount and Specie on Swelling

In addition to direct adsorption of water by clays, repulsion of adjacent double layers also affects the swelling of clays (Baver et al.

1972). Cations attracted to the negative charges in clay particles are concentrated near the clay surface and decrease in concentration with distance from the particle. A diffuse double layer thus occurs consisting of the negatively charged clay surface and the diffuse concentration of balancing cations. Factors which influence the thickness of the double layer, such as exchangeable cation valence and effective size, and ion concentration in the bulk solution also affect the degree of intra-particle swelling. These factors are discussed more fully below.

Baver and Winterkorn (1935) observed the effect of cation species on the swelling of a soil material when they calculated the relative swelling of a beidellite-illite type clay saturated with Li^+, Na^+, and Ca^{++} to be 5.5, 4.4, and 1.0, respectively. Low (1961) explained these data as due to the hydration of adsorbed cations which breaks up the structure of the water films adsorbed on clay surfaces. Another explanation of the results observed by Baver and Winterkorn might be that addition of Li^+ and Na^+ expanded the double layer because of their large hydrated radii and low valence compared to Ca^{++}, thus increasing the repulsive force between the clay particles. In the same paper, Low observed that dissociated exchangeable cations lower the activity of water near the clay surface in much the same way as ions lower the activity of water in solution, giving rise to an osmotic attraction of water by clays. Fink and Thomas (1964) offered virtually the same

explanation for the phenomenon of "osmotic" swelling of clays. They observed that cations with high hydration energies will be located farther from a clay surface than will be cations with lower hydration energies due to the difference in thickness of the water hulls surrounding the hydrated cations. The coulombic force of attraction between clay surface and cation will decrease with distance. Water can thus move more freely between the clay surface and a highly hydrated cation, preserving the water structure from the clay surface to a greater distance from that surface and resulting in swelling. They concluded that clays saturated with a highly hydrated cation, such as Na^+, will experience more osmotic swelling than will clays saturated with cations which may be partially dehydrated by strong electrostatic attraction to the surface, such as Ca^{++}. DuPlessis (1969) also observed that a decrease in ionic hydration is accompanied by a decrease in colloid swelling. It can be concluded on the basis of the above arguments that the exchangeable sodium percentage (ESP) will have a direct effect on the degree of swelling of a soil material because Na^+ both promotes osmotic swelling and expands the double layer.

The concentration of soluble cations is another factor which influences the swelling of soil materials. Baver (1930) reported that flocculation, an opposite of the swelling process, occurred when sufficient soluble salts were present in the soil solution. Norrish (1954) observed that interlayer expansion of swelling clays beyond 35Å

is continuous and linearly related to the reciprocal square root of the normality of the external solution ($N^{-\frac{1}{2}}$). Hemwall and Low (1956) determined that a net hydrostatic or osmotic repulsive pressure results when the ion concentration in the median plane between two parallel clay plates exceeds that in the external solution.

Effect of Clay Mineralogy on Swelling

Interlayer and macroscopic swelling are two types of swelling discussed in the literature. Interlayer swelling is a two-step process, the first of which is the stepwise hydration of interlayer surfaces and cations, and the second then being the continuous swelling previously discussed by Norrish (1954). Interlayer swelling is a reversible process as the clay platelets maintain a parallel orientation throughout the process. Macroscopic swelling, on the other hand, occurs not only between individual clay platelets but between clusters of clay platelets as well.

Demixed and mixed ion models have been proposed to explain the two types of swelling behavior in mono and divalent cation clays. The demixed model is applicable only to clays having internal exchange sites. Shainberg and Kemper (1966) offered the following explanation of the demixed ion model: Although Ca^{++} and Na^{+} have similar mobilities in solution, Ca^{++}, because of its divalent charge, has a much lower mobility than Na^{+} near the clay mineral surfaces. In a bi-ionic

system, the less mobile cation Ca^{++} will occupy internal exchange sites, while Na^+ will dominate the remaining (external) sites by default. The demixed ion model predicts clays to consist of a mixture of homo-ionic Ca^{++} saturated interlayers and Na^+ saturated interlayers and external surfaces, with only the Na^+ regions exhibiting interlayer swelling (McNeal 1970). Calcium saturated interlayers tend to adsorb only three layers of water (Blackmore and Miller 1961), while Na^+ saturated interlayers tend to adsorb additional water osmotically (Norrish and Quirk 1954). The result of ion sorting is the formation of "tactoids" or stacks of clay platelets no thicker than 1 μm (Mills and Zwarich 1973). Shainberg and Kaiserman (1969) verified the existence of tactoids through light transmission studies of Ca^{++} and Na^+ montmorillonite suspensions. Mills and Zwarich (1973) determined that bentonite tactoids under a particular set of experimental conditions consisted of 12 clay platelets, each 19 Å thick for a total thickness of .230 μm. The sorting of ions of different valences has been demonstrated only for the internal surfaces of clays.

The mixed ion model predicts that individual clay surfaces consist of a mixture of exchangeable ion species. According to the mixed ion model, continuous swelling occurs both between the internal and external surfaces of clay particles with the amount of swelling depending, among other things, upon the relative amounts of Na^+ and Ca^{++} present. Even if some demixing does occur, this model is applicable to illite and

kaolinite clays because kaolinite has virtually no internal exchange sites and most internal exchange sites of illite are bound up by K^+ (Baver et al. 1972).

The ESP of a montmorillonite tactoid saturated internally with Ca^{++} and externally with Na^+ is low because of the low proportion of external surfaces of this mineral. According to the literature, external surfaces may be completely saturated with Na^+ at ESP values as low as 15 and appreciable interparticle swelling can occur (Shainberg et al. 1971). This is a possible explanation for the common dividing line between sodic and non-sodic soils (U. S. Salinity Laboratory Staff 1954). The demixed ion model thus explains the hypersensitivity of montmorillonite to Na^+.

Hydraulic Conductivity

Hydraulic conductivity (K) is a measure of the ability of the soil to transmit water (Black 1965) and has been found to be a function of the pore size as well as distribution within a sample (Marshall 1958). The dispersing effect of Na^+ generally reduces the hydraulic conductivity of a sample (Brooks et al. 1956, Reeve 1957, Waldron and Constantin 1968). McNeal and Coleman (1966) postulated that the decrease in conductivity following an increase in sample ESP can result both from particle dispersion and from the closing of pores by interlayer swelling. Dixit and Lal (1972) reported that an increase

in exchangeable Na^+ from 0-30% decreased the K values of soils of six

different textural classes from a mean of 2.79 to a mean of .16 cm/hr.

Modulus of Rupture

Soil modulus of rupture (MOR) values have been reported to be

sensitive to additions of both Ca^{++} and Na^+ (Dollhopf 1975, Moe et al.

1971, Richards 1953). Two different sources have reported MOR values

to increase linearly with increasing exchangeable Na^+ (Brooks et al.

1956, Reeve et al. 1954).

Coefficient of Linear Extensibility

A high degree of correlation exists between the shrink-swell

potential of soils or soil components and the ESP of the soil (Waldron

and Constantin 1968 and 1970, McNeal et al. 1966, Davidson and Page

1956, Reeve et al. 1954). Coefficient of linear extensibility (COLE)

values are often used to monitor the physical changes that occur at

various soil ESP values.

Anderson et al. (1973) found COLE values of soil materials to be

highly correlated (R^2 = .938) with the combination of % fine clay and

the sample ESP. The R^2 value for fine clay alone was found to be .863,

whereas that for ESP alone was only .323. McCormack and Wilding (1975)

found COLE values to be highly correlated with total clay content

(R^2 = .93). Franzmeier and Ross (1968) determined COLE values of 0 to

.03 between the 1/3 bar moisture content and oven drying to be non-

critical, .03 to .06 marginal, .06 to .10 critical, and values greater

than .10 to be very critical in terms of soil material swelling

potentials. They found kaolinite and illite samples to have COLE

values less than .03, whereas montmorillonite samples generally had

values greater than .03. They also determined that soils with clay

fractions dominated by montmorillonite (>50%) generally respond as if

their clay fraction was composed solely of montmorillonite.

MATERIALS AND METHODS

Experimental Design

Overburden samples ranging in depth from .6 to 72 meters (2 to
235 ft) from proposed coal mine sites in eastern Montana and western
North Dakota were used in this research. Samples having clay fractions
dominated by smectite, illite, or kaolinite were identified by the
Montana Agricultural Experiment Station in previous studies by the
use of X-ray diffraction techniques. Four or five overburden samples
representative of each clay type were used in the experiments. Clay
percentages were identified by pipette analysis. The widest range in
particle size distribution available was chosen within each minera-
logical sample group. Table 1 lists some physical and mineralogical
properties of the samples used in this research. Table 2 shows the
experimental design including the samples and the number of replica-
tions of each sample used in the individual experiments.

Inducing Exchangeable Sodium Percentages

A range of exchangeable sodium percentage (ESP) values was imposed
on each sample used in this research to monitor changes in physical
properties resulting from changes in ESP values. The United States
Salinity Laboratory has determined that at low values (<30) a near-
linear relationship exists between the equilibrium ESP of a sample
and the sodium adsorption ratio (SAR) of the sample solution (1954).
By forcing a solution of known SAR through a sample, the ESP of the

Table 1. Physical and mineralogical sample properties.

Sample #	Depth	Sand	Silt	Clay	Textural class	Smectite	Illite	Kaolin- ite	Quartz	Vermic- ulite	Chlorite
	m	--------%-----									
Kiewitt A	.	71	18	11	SL	4	T	T	T	–	T
531	13.7-15.2	66	18	16	SL	4	T	T	T	T	1
45246	.6- 1.5	33	43	24	L	3	1	T	T	–	T
45250	6.0- 7.6	11	63	26	SiL	3	1	T	T	–	1
45254	12.2-13.4	36	48	16	L	3	1	1	–	–	1
8	10.4-13.7	6	56	38	SiCL	T	4	1	T	T	T
9	13.7-19.2	34	36	30	CL	T	3	2	T	–	1
11	29.6-31.1	32	41	27	L-CL	–	4	1	T	–	T
12	32.0-35.4	22	51	27	SiL-CL	T	4	1	T	–	T
18	63.7-71.6	33	48	19	L	–	3	2	–	1	1
44534	37.8-39.3	64	26	10	SL	–	2	3	–	–	T
44535	39.6-41.1	18	65	17	SiL	–	2	3	–	–	–
44540	48.8-50.6	14	70	16	SiL	–	2	3	–	–	1
45263	41.1-42.7	81	16	3	LS	–	1	4	–	–	–
45266	45.1-46.6	17	65	18	SiL	–	2	3	T	–	1

* T = 0- 5%   1 = 6- 25%   2 = 26-50%   3 = 51-75%   4 = 76-100%

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Table 2. Experimental design.

|	Hydraulic Conductivity						Shrinkage of Briquets				Modulus of Rupture				Coefficient of Linear Extensibility			
	reps	SAR 0	5	10	15	20	SAR 0	5	10	15	SAR 0	5	10	15	SAR 0	5	10	15
Kiewitt A	3 reps	4	3	4	—		2	2	2	2	2	—	2	2	2	2	2	2
531	4 reps	3	3	4	—		2	2	2	2	2	—	2	2	2	2	2	2
45246	4 reps	4	3	4	—		2	2	2	2	2	2	1	1	2	2	2	1
45250	3 reps	4	3	4	—		2	2	2	2	2	2	—	—	2	2	—	2
45254	3 reps	4	4	4	—		2	2	2	2	2	2	—	—	2	—	1	2
8	4 reps	—	4	4	—		—	—	2	2	—	—	2	2	2	—	2	2
9	3 reps	—	3	4	—		—	—	2	2	—	—	2	2	2	—	2	2
11	2 reps	—	3	3	—		—	—	2	2	—	—	2	2	2	—	2	2
12	3 reps	—	3	3	—		—	—	2	2	—	—	2	2	2	—	2	2
18	4 reps	—	3	4	—		—	—	2	2	—	—	2	2	2	—	2	2
44534	3 reps	—	4	4		—	2	—	1	2	2	—	2	2	2	—	2	—
44535	3 reps	—	4	4		1	1	—	1	1	2	—	1	1	1	—	—	2
44540	4 reps	—	3	4		2	1	—	1	1	2	—	2	2	1	—	2	—
45263	3 reps	—	3	3		—	2	—	1	1	2	—	2	1	—	—	—	—
45266	4 reps	—	4	4		4	—	—	—	—	—	—	—	—	2	—	2	2

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sample can be raised or lowered to a predictable value. A minimum of 1 liter of solution having electrical conductivity of 4.0 mmhos/cm and known SAR was forced through each replication of each sample under hydraulic head of about 1.75 meters. Samples were washed with distilled water for five days or until a minimum of 1 liter of water had passed through to remove soluble salts. They were then tested for hydraulic conductivity, briquet shrinkage, and modulus of rupture. Initial results of linear extensibility tests were considered random enough to merit sodium resaturation. Samples were dry-ground and sieved to limit particle size to ≤ 1 mm in diameter. Crushed samples weighing 50 to 75 grams were washed four times with solutions of various SAR values and an electrical conductivity of 4.0 mmhos/cm. They were leached with 200 to 500 ml of distilled water to remove soluble salts and were then used in the linear extensibility tests.

Hydraulic Conductivity

Hydraulic conductivity was used in this research as a means of quantifying the physical changes that occurred in samples over a range of ESP values.

The conductivity apparatus can be seen in Figure 1. The sample container was perforated on the bottom to allow passage of water through the sample which was crushed and sieved to <1 mm in size. The container was covered on top and bottom with Whatman #40 filter paper.

FIGURE I

HYDRAULIC
CONDUCTIVITY
APPARATUS
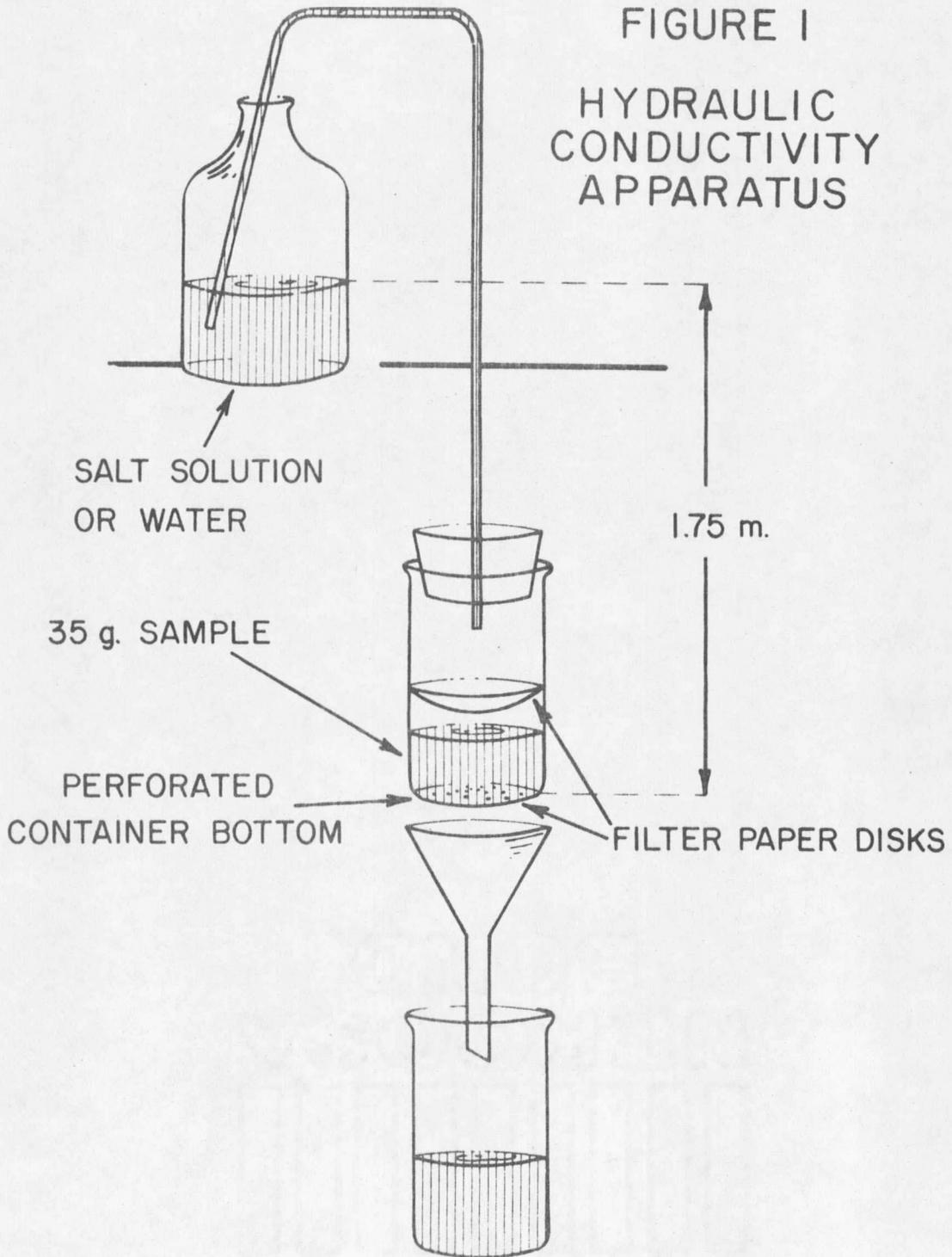
The hydraulic head was raised to a uniform height by filling the upper
bottles with distilled water. The amount of water flowing through the
sample per unit time was then measured. The equation used to cal-
culate the hydraulic conductivity (K) of the samples was

$$K = (Q/At)(L/\Delta H) \qquad \text{(Black 1965)}$$

where Q is the volume of water passing through the sample in a known
time t. A is the cross-sectional area of the sample, L is the length
of the sample, and ΔH is the hydraulic head.

COLE Tests

Coefficient of linear extensibility (COLE) is a measure of the
shrink-swell potential of a soil. Calculation of COLE involves a
measurement of the 1-dimensional length change between two moisture
contents of a Saran-coated natural ped or clod.

In most cases, the standard COLE procedure was not suitable for
this research because there were no soil peds or clods of material
available. Samples were already crushed and sieved upon receipt.
Schafer and Singer (1976) developed an alternative method of measuring
COLE. The Schafer and Singer method involves a measurement of the
1-dimensional length change upon drying of rods formed from pastes of
soil material near saturation. The $COLE_{rod}$ procedure was found to
be highly correlated to the standard COLE procedure (R^2 = .83) and was
more suitable for this research. Rods formed from pastes just below

a saturated condition 1 cm in diameter and 9-12 cm long were extruded onto a ceramic plate as shown in Figure 2. The rods were then allowed to air-dry. The change in length between the wet and dry rods was measured and the linear extensibility between 0 to 1/10 bar and air-dry moisture tensions was calculated by the equation

$$COLE_{rod} = (1_m - 1_d)/1_d \qquad \text{(Schafer and Singer 1976)}$$

where 1_m and 1_d represent the moist and dry rod lengths, respectively.

Modulus of Rupture

Modulus of rupture is a measure of the minimum force necessary to break a specially-molded briquet of soil material. This test gives an indication of the crusting strength of specific soil materials (Richards 1953).

The technique of modulus of rupture used in this research was similar to that described by the United States Salinity Laboratory Staff (1954) except that the briquet molds were filled with a saturated paste. First attempts at making briquets according to the United States Salinity Lab procedure gave unsatisfactory results. Cracks formed in the briquets rendering them useless for testing crusting strength. Usable briquets resulted when molds filled with saturated pastes were allowed to dry for two months in a 95% relative humidity chamber composed of an airtight tub, the bottom of which contained