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HEAT OF WETTING OF SOILS

M. B. RUSSELL AND L. A. RICHARDS

Many important soil processes such as base exchange capacity, plant food availability and moisture holding capacity, are influenced by the amount of surface per unit mass of soil. For this reason, measurements related to this soil characteristic may be used in connection with many soil problems. This article is concerned with the description of a method of measuring the relative surface area of soils with apparatus suited for student use. It consists in measuring the heat energy liberated by a dry soil which is wetted by water at the same temperature.

The phenomenon of liberation of heat when dry powders are wetted was observed as early as 1802 by Leslie whose observations were confirmed and reported by Pouillet (11). With the growth of colloidal chemistry this so-called heat of wetting came to be regarded as a method of determining the total surface and has been used widely in studies of silica gel. About 1900 Mitscherlich (8) applied this measurement to soil but abandoned it in favor of hygroscopicity determinations as an indication of soil surface. In 1924, Bouyoucos (4) and Anderson (1) published articles on the suitability of heat of wetting measurements as a means of estimating the colloidal content of soil. Since 1924 numerous articles (3, 5, 6, 7) have been published both in this country and abroad in which the heat of wetting has been used as a measure of soil surface.

The apparatus to be described in this paper is a modification of that designed by Patrick and Grimm (10) for silica gel studies. The changes in design have been introduced in an effort to make the apparatus more suitable for student use without sacrificing precision.

The determination is made in a pint thermos bottle (1) shown in Fig. 1. Temperature changes are measured with a 5° Beckmann thermometer (2). The soil water mixture is mixed by an agitator (4) containing an electric heating coil in the brass case (3). The soil is held in a brass bucket (5) which is shown in detail in Fig. 2. The bucket is equipped with a spring-operated lid which opens when the bucket is inverted. A spring (9) holds the bucket in an

Published by UNI ScholarWorks, 1938 179

180

IOWA ACADEMY OF SCIENCE [Vol. XLV

upright position prior to dumping which is accomplished by pulling on a copper wire (8) that is attached to the bottom end of the bucket. The whole bucket is held in a brass hanger (6) which is fastened to the end of the fiber tube (7) that leads out of the vacuum bottle through a three-hole cork (10).

The following procedure is used in determining the heat of

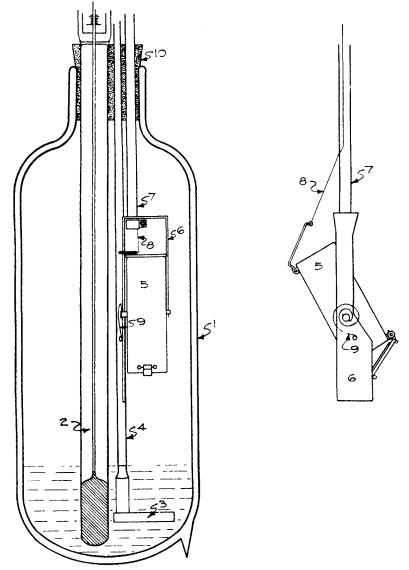


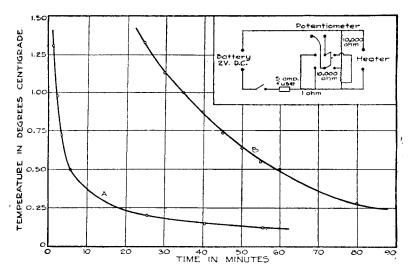
Fig. 1. Diagrams showing the arrangement of the soil bucket, a thermometer and heating element within the vacuum flask. At the side, the bucket is shown in the inverted position for dumping the soil.

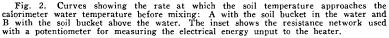
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181



HEAT OF WETTING OF SOILS





wetting: Fifty cubic centimeters of distilled water are placed in the vacuum bottle. Ten grams of soil that have been dried at 110°C. for 18 hours are weighed into the soil bucket. The agitator, soil bucket, and thermometer are then introduced into the vacuum bottle in the order named. The soil bucket, still in an upright position, is lowered until its lower end is in contact with the water. After 45 minutes the soil bucket is raised from the water and the temperature is recorded. The soil is dumped and the mixture agitated until a new constant temperature is reached. This is recorded. The water equivalent of the calorimeter is determined by measuring the temperature rise resulting from the addition of a known quantity of electrical energy. Several measurements of voltage and current are made during the measured heating time.

The resistance box is used in connection with a potentiometer for measuring the voltage and current supplied to the heater. The current is measured in terms of the IR drop across a standard one ohm resistor which is placed in series with the heater. The voltage is measured by doubling the IR drop measured across one of the two 10,000 ohm resistors which are connected in series with each other but in parallel with the heater.

It is important that the soil and water be at the same temperature before mixing if true values of the heat of wetting are to be obtained. The length of time required to reach such a thermal

Table I -- Table Showing the Relation Between Mechanical Analysis and Heat of Wetting

	Mechanical Analysis					Heat of Wetting			Total	Area
Soil	Coarse Sand 2.0-0.2mm	Fine Sand 0.2-0.02mm	Silt 0.02- .002mm	Clay < .002mm	Organ- ic Mat- ter	lst Trial	2nd Trial	Aver- age	Surface Area * m ²	Heat of Wet- ting
	Percentage									
Dickinson fine sand	33.3	48.1	9.8	6.7	2.1	1.04	1.02	1.03	2.34	2.27
Clarion sandy loam	18.5	31.1	28.6	18.8	3.0	2.25	2.18	2.21	5.79	2.62
Marshall silty clay loam	0.4	2.2	62.6	3 1.2	3.6	4.21	4.10	4.16	9.51	2.28
Wabash silty clay	0.7	5.0	48.2	40.2	5.9	6.72	6.79	6.76	12.13	1.80
Sharkey clay	2.6	2.0	33.4	56.5	5.5	8.27	8.09	8.18	15.75	1.93

* The organic matter was included as clay.

182

Russell and Richards: Heat of Wetting of Soils HEAT OF WETTING OF SOILS

1938]

equilibrium was determined by placing one junction of a copperconstantan thermocouple in the soil bucket and the other in the water. Measurements of the thermal e.m.f. of the couple at various time intervals indicate that if the soil bucket is partly submerged in the water, the temperature difference after 45 minutes is insufficient to cause a 1 per cent error in the heat of wetting. If the bucket is suspended above the water, several hours are required before the temperature difference reaches a negligible value.

Table I shows the results of duplicate determinations of the heat of wetting of five soils ranging in texture from a fine sand to a clay. Data are also included in Table I showing the mechanical analyses of the soils as determined by the pipette method. The data indicate that there is some relation between texture and heat of wetting and that low values of the latter are associated with coarse texture and higher values are obtained on soils having higher contents of silt and clay. The use of heat of wetting values for the estimation of the colloidal content of soils can be made only after the heat of wetting of the extracted colloid is known since it has been shown by Baver (2) and Hoseh (5) that different colloids vary in their heats of wetting. Pate (9) investigated the influence of the amount and nature of the replaceable bases upon heat of wetting and found that a low heat of wetting was usually associated with a high content of monovalent cations.

If the heat of wetting were dependent upon particle size alone the quotient, total area/heat of wetting would be a constant for all soils. By assuming that the soil particles are spherical and have a uniform size distribution we have calculated the total area that would be represented by ten grams of each of the soils in an ovendry condition. The density of the particles was taken as 2.61 gm/cm³. The quotient, total area/area of wetting, while not a constant for the five soils, is in each case of the same order of magnitude. This indicates that surface area is probably the primary soil characteristic influencing the heat of wetting.

There have been two principal theories advanced to explain the cause of heat of wetting. The first theory states that the first layers of water that wet the dry material are bound so tightly to the solid that they are compressed and in the process liberate energy. On the basis of the compression theory the heat of wetting should be negative at temperatures between 0° and 4° C. In their measurements on silica gel, Patrick and Grimm (10) found the heat of wetting to be positive over this temperature range. These work-

5

ers, therefore, advanced the surface energy theory in which the energy liberated is attributed to the great reduction in the area of the air-water interface that accompanies the wetting process. It is thought that the entire soil surface is covered by a thin water film which accounts for an air-water interfacial area practically equal to the total surface area of the soil. When the soil is wetted this large interface is destroyed since a water-water interface cannot exist. If the soil is wetted with an organic liquid the interface is not destroyed but the interfacial surface tension is changed from that of an air-water interface to that of an organic liquid-water interface. Consequently, the heat of wetting is larger or smaller than that observed with water, depending on whether this change is greater or less than that represented by the complete destruction of the interface.

Patrick and Grimm give the following expression for surface energy (E) in ergs/cm²

$$\mathbf{E} = \boldsymbol{\omega}\boldsymbol{\sigma} - \mathbf{T} \, \frac{\mathrm{d}\boldsymbol{\sigma}}{\mathrm{d}\mathbf{T}} \, \boldsymbol{\omega}$$

where ω represents surface area, σ surface tension and T absolute temperature. On the basis of this equation Patrick and Grimm calculated the surface area necessary to produce the heat of wetting that was observed and found it to agree well with observed particle sizes.

CONCLUSIONS

1. An apparatus is described for measuring the heat of wetting of soils.

2. Experimental errors accompanying the determination are reduced to the order of magnitude of the errors inherent in the method of sampling.

3. Heat of wetting varies with texture since the total soil surface seems to be the most important factor influencing the amount of energy liberated. Other workers have pointed out that the $SiO_{2}/R_{2}O_{3}$ ratio and the nature and amount of exchangeable bases also exert an influence.

4. Surface energy changes seem adequate to account for the heat of wetting.

5. Since heat of wetting values are influenced by a number of experimental factors, standardization of technique is recommended if consistent results are to be obtained.

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