Experiment Study on Determination of Surface Area of Fine-grained Soils by Mercury Intrusion Porosimetry

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Abstract. The specific surface area (SSA) has a great influence on the physical and chemical properties of fine-grained soils. Determination of specific surface area is an important content for fine-grained soils micro-meso analysis and characteristic research. In this paper, mercury intrusion porosimetry (MIP) was adopted to determine the SSA of fine-grained soils including quartz, kaolinite, bentonite and natural Shenzhen soft clay. The test results show that the average values of SSA obtained by MIP are 0.78 m$^2$/g, 11.31 m$^2$/g, 57.28 m$^2$/g and 27.15 m$^2$/g respectively for very fine-grained quartz, kaolin, bentonite and natural Shenzhen soft clay, and that it is feasible to apply MIP to obtain the SSA of fine-grained soils through statistical analysis of 97 samples. Through discussion, it is necessary to consider the state of fine-grained soils such as pore ratio when the SSA of fine-grained soils is determined by MIP.

1. Introduction

The specific surface area (SSA) is a property of solids defined as the total surface area of porous materials per unit volume or unit mass. The former is volume specific surface area(units of m$^2$/m$^3$ or m$^{-1}$), and the latter is mass specific surface area (with units of m$^2$/kg or m$^2$/g).

The SSA of soil is closely related to its macro mechanical properties. For many materials, when particle size is reduced to 1 or 2μm or less, the surface forces begin to exert a distinct influence on the behavior[1], and physical and chemical properties such as permeability and rheological properties may be greatly influenced by the SSA for soils, especially fine-grained soils[2]. It is necessary to determine the SSA for giving a reasonable explanation of various engineering properties of fine-grained soils from the micro level.

Laboratory test of SSA mainly includes adsorption method, which can be divided into liquid and gas adsorption[3,4]. The former includes glycerol method, ethylene glycol method, EGME method, methylene blue method and mercury intrusion porosimetry. The latter includes BET method, steam method, and so on. Mercury intrusion porosimetry with application of the state-of-the-art instruments can measure the specific surface area of porous materials by measuring the pore distribution of porous materials[5,6].

In this paper, mercury porosimetry (MIP) was used to test the SSA of very fine-grained soil, including bentonite, kaolin, quartz and natural Shenzhen soft clay. Then the effectiveness and
applicability of mercury intrusion porosimetry for determination of the SSA of fine-grained soils were discussed and analyzed.

2. MIP

2.1. Principle of Test
Mercury intrusion porosimetry (MIP) is based upon the principle that a non-wetting fluid, such as mercury, does not intrude a porous medium, unless an external pressure is applied. Assuming pores are cylindrical capillaries, the relationship between the intrusion pressure and the size of the entrance pore radius was given by Washburn equation (1921) as:

$$p = \frac{-2\sigma \cos \theta}{r}$$

(1)

Where \(p\) is the intrusion pressure; \(r\) is the entrance or throat pore radius; \(\sigma\) is the surface tension of the intrusion liquid; \(\theta\) is the contact angle between the intrusion liquid and the porous medium.

Mercury intrusion porosimetry can be used to determine the specific surface area of soils. The total surface area of soil is calculated using formula (2) after MIP test:

$$S = \frac{1}{\sigma \cos \theta} \int_{0}^{V_{\text{max}}} pdV$$

(2)

A sample with a mass of \(M\) is obtained from the total surface area, and the mass specific surface area (with units of \(m^2/kg\) or \(m^2/g\)) is:

$$S_M = \frac{1}{\sigma M \cos \theta} \int_{0}^{V_{\text{max}}} pdV$$

(3)

2.2. Test Procedure
AutoPore IV 9510 Automated Mercury Porosimeters produced by the United States Micromeritics company was used. The pore diameter range that can be measured by the equipment is from 3nm to 350μm. The whole test operation process was carried out in accordance with the requirements of the relevant operating procedures [5-7].

2.3. Drying Methods
Drying process is an important part of the mercury intrusion porosimetry. The dehydration methods are used in this test including in air-drying, oven-drying and freeze-drying [7].

3. Test Soil Samples

3.1. Property of Soil Sample

| samples       | Specific gravity | Liquid limit (%) | Plastic limit (%) | Plasticity index | Surface area mean particle size (μm) |
|---------------|------------------|------------------|-------------------|------------------|-------------------------------------|
| quartz        | 2.74             | 16.8             | 11.1              | 5.7              | 3.92                                |
| kaolin        | 2.67             | 42.6             | 27.4              | 15.2             | 2.321                               |
| bentonite     | 2.58             | 271.7            | 59                | 212.7            | 3.051                               |
| Shenzhen soil | 2.71             | 69.6             | 30.1              | 39.5             | —                                   |
Table 2. Ingredient and proportion of natural Shenzhen clay

| Ingredient          | Montmorillonite (%) | Illite (%) | Kaolinite (%) | Quartz (%) | Potash feldspar (%) | Soda feldspar (%) | Halite (%) |
|---------------------|---------------------|------------|---------------|------------|--------------------|-------------------|------------|
| Proportion          | 14.5                | 26         | 29.2          | 20.3       | 4.6                | 3.4               | 2          |

The selected soil samples are artificial fine-grained soils prepared with high purity ultra-fine powder including quartz, kaolin and bentonite [8]. In addition, natural Shenzhen soft soil [9] is also selected. The main parameters of the high-purity superfine powder and natural Shenzhen soft soil sample are shown in Table 1. The main mineral compositions of natural soil samples in Shenzhen are shown in Table 2.

3.2. Soil Samples Preparation

The high-purity ultra-fine artificial soil powder was used in this experiment. The artificial samples were prepared with impact compaction method according to Standard for Soil Test Method (GB/T50123-1999) [7,10].

4. Experimental Results and Analysis

4.1. Test Results

![Cumulative Intrusion vs Pressure curves of quartz (e=0.8)](image1)

**Figure 1. Cumulative Intrusion vs Pressure curves of quartz (e=0.8)**

![Cumulative Intrusion vs Pressure curves of kaolin (e=1.6)](image2)

**Figure 2. Cumulative Intrusion vs Pressure curves of kaolin (e=1.6)**
Mercury intrusion porosimetry was carried out on the soil samples after drying, and the Cumulative Intrusion vs Pressure curves of four different component soil samples were shown in Figure 1 to Figure 4. The abscissa of the curve is mercury injection pressure, and the vertical axis of curve is cumulative intrusion mercury per gram of soil under a certain pressure. Using the formula (3), the SSA of each soil sample can be obtained by integrating the cumulative intrusion vs pressure curve.

According to test results, SSA of saturated quartz with void ratio 0.8 is 0.789 m²/g, SSA of saturated kaolin with pore ratio 1.6 is 11.140 m²/g, SSA of saturated bentonite with pore ratio 1.6 is 50.118 m²/g, and SSA of saturated natural Shenzhen soft clay with pore ratio 1.6 is 26.202 m²/g. The experiment results show that the SSA of quartz is the smallest. Because quartz crystals are often developed into intact columnar crystals without lamellar structure, even for extremely fine granular quartz, the SSA is still very low. The main mineral compositions of kaolin and bentonite are kaolinite and montmorillonite respectively, and both of them have a layered structure, so their SSA is larger than quartz. The composition of natural Shenzhen soil contains minerals such as kaolinite, montmorillonite and quartz (see Table 2), so the SSA value of natural Shenzhen soil obtained by MIP is between the SSA value of kaolin and the SSA value of bentonite.

4.2. Variability Analysis

Generally speaking, the specific surface area of soils is related to their composition, and the SSA obtained by MIP of four kinds of soil samples with different composition is statistically analyzed. The results are shown in table 3.
Table 3. Statistical analysis of the specific surface area of fine-grained soils by MIP

| Soil samples | quartz | kaolin | bentonite | Shenzhen soil |
|--------------|--------|--------|-----------|---------------|
| Statistic number | 18     | 10     | 47        | 22            |
| average value (m$^2$/g) | 0.78   | 11.31  | 57.28     | 27.15         |
| Maximum value (m$^2$/g) | 0.83   | 12.05  | 69.26     | 30.68         |
| minimum value (m$^2$/g) | 0.72   | 10.43  | 43.73     | 24.95         |
| standard deviation | 0.03   | 0.61   | 6.53      | 1.50          |
| Coefficient of variation | 0.04   | 0.05   | 0.11      | 0.06          |

Table 3 shows that the SSA of different composition soil sample is different, and the SSA value of soil sample with the same composition fluctuates within a certain range. That is because the SSA of porous materials depends on the inner pore structure, while fine-grained soils of different moisture content, saturation, pore ratio and drying methods would lead to different pore structure which causes the errors of test results. In other words, even if the soil samples have the same composition, the test errors exist in the SSA of fine-grained soils by MIP due to the different soil state. Despite these errors, it can be seen from table 3 that the variation coefficients of SSA by MIP are 0.04, 0.05, 0.11 and 0.06 respectively for quartz, kaolin, bentonite and Shenzhen soft soil. The low variation coefficient indicates that the MIP is feasible for determining the SSA of fine-grained soils because of good repeatability.

4.3. Discussion on Suitability

As porous medium, the pore size distribution range of fine-grained soils is extremely wide. The specific surface area of fine-grained soils was measured by mercury intrusion porosimetry with pore diameters range from 3nm to 350 $\mu$m, so the SSA of soil with pore diameter less than 3nm and larger than 350 $\mu$m can not be measured by mercury intrusion porosimetry.

In addition, the SSA of porous materials is based on the pore size distribution through mercury intrusion porosimetry. Even the soil samples with the same composition, the pore size distribution of soil may change with different moisture content, saturation, pore ratio and drying method, so the SSA of soil may change with varying pore size distribution. Therefore, it is necessary to consider the state of the soil, such as pore ratio and saturation, when the SSA is obtained by MIP.

5. Conclusions

1. The average values of SSA obtained by MIP are 0.78m$^2$/g, 11.31m$^2$/g, 57.28m$^2$/g and 27.15m$^2$/g respectively for very fine-grained quartz, kaolin, bentonite and natural Shenzhen soft clay.

2. The SSA data measured by mercury intrusion porosimetry have good reproducibility and small variability and it is feasible to apply mercury intrusion porosimetry to obtain the SSA of fine-grained soils.

3. It is necessary to consider the state of soil, such as pore ratio and saturation, when mercury intrusion porosimetry is used to determine the SSA of the fine-grained soils.

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