Pore space studies on Wartanian glacial till (Central Poland) polluted with petrol and diesel oil, based on mercury porosimetry

Dorota IZDEBSKA-MUCHA


Air-dried samples of glacial till were polluted in the laboratory with petrol and diesel oil. A comparative analysis of natural and contaminated material was made on the basis of mercury porosimetry measurements. The investigation revealed relatively slight changes in the pore space of the polluted samples, which were associated with adsorption of hydrocarbons onto the soil particles rather than with microstructural change. Introduction of non-polar organic fluid into soil pores did not cause rearrangement of the natural soil structure.

Due to the initial air-dried state of the soil material, these findings pertain to unsaturated soils only. These results contribute to the crucial, but still poorly recognized problem of the engineering geology properties of organic contaminated soils.

Dorota Izdebska-Mucha, Faculty of Geology, Warsaw University, wirki i Wigury 93, PL-02-089 Warszawa, Poland; e-mail: dim@uw.edu.pl (received: November 27, 2006; accepted: October 18, 2007).

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INTRODUCTION

Nowadays one of the most important problems in environmental protection and land development planning is the increasing pollution of the water-soil system by toxic chemicals. The main sources of these are: landfill effluents, industrial sewage, fertilizers, herbicides, pesticides and last but not least, petroleum and its products. According to a report of the Chief Inspectorate for Environmental Protection (GIOS), in 1998 in Poland petroleum leakages made up about 39% of accidents that might have been extremely hazardous for the environment (Warchalowska, 1999).

Petroleum pollution of soil is not only dangerous for the ecosystem but also has a profound influence on its engineering geology properties. In this respect, many studies have been conducted to evaluate the effects of organic liquids on physical, strength and filtration parameters of contaminated soils (e.g., Brown et al., 1984; Fernandez and Quigley, 1985; Korzeniowska et al., 1995; Barański, 2000; Korzeniowska-Rejmer, 2001; Zadroga and Olańczuk-Neyman, 2001; Anandarajah, 2003; Izdebska-Mucha, 2003, 2005; Račkauskas, 2003; Khamenechiyan et al., 2007). Researchers have reported increases in hydraulic conductivity, settlement and liquidity index and decreases in shrinkage, swelling, angle of internal friction and cohesion in soils polluted with organic substances. The degree of alteration depended on the soil type, its water content, and the concentration of and exposure time to the pollutant.

Migration of pollutants in soil is governed by several factors, which one may split into three general groups: (1) soil structure and microstructure, (2) fluid properties and (3) physico-chemical interactions associated with the solid — liquid phase contact. Due to specific interactions between clay minerals and chemicals, the soil fabric is supposed to undergo changes when gets polluted. Kaya and Fang (2000) showed that attractive and repulsive forces between clay particles decrease as the dielectric constant of the pore fluid decreases, which results in flocculation of soil particles and formation of clusters that act like silt-sand grains. This effect was supported by microscopic images of the polluted soils (Fernandez and Quigley, 1985; Kaya and Fang, 2005). The images revealed that in the environment of organic liquid the clay soils were highly flocculated, more porous, and contained more macropores in comparison to water-saturated samples. Based on visual examination of soils leached with organic fluids, formation of cracks was observed (Anandarajah, 2003).

These findings do not, however, deliver a quantitative evaluation of the soil microstructure changes. Thus, the aim of this
The study was quantitative assessment of pore structure alteration of clayey soil that was subjected to petroleum contamination. For the purpose of the study the mercury porosimetry technique was applied. Measurements were conducted in the Polish Geological Institute, Hydrogeology and Engineering Geology Department.

**MATERIALS AND METHODS**

Quaternary glacial till samples* of the Wartanian Glaciacion were examined. The samples were collected from a brickyard pit in Budy Mszczonowskie near Mszczonów (Fig. 1). A lithological profile of the pit (Fig. 2) shows two series of glaciofluvial deposits separated by the glacial till layer analysed. The lower glaciofluvial deposit comprises fine-grained sand. The upper one comprises medium-grained sand with gravel. Particle size distribution analysis showed that all the glacial till samples are made of sandy clay with silt, according to British Standard classification (BS1377: Part 2:1990).

Using Setaram Labsys TG-DTA/DSC 1600 device, thermogravimetrical analysis was conducted to determine the mineralogical composition of the till samples. Quantitative calculations were made according to the method of Kościówko and Wyrwicki (1996) and Wyrwicki (1988). The data obtained

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*Symbols of soil samples used in this paper: G 1, G 2, G 3, G 4, G 5 — symbols of till samples collected; G NS — average values of the parameters considered of undisturbed samples; G B — average values of the parameters considered of samples saturated with petrol; G ON — average values of the parameters considered of samples saturated with diesel oil.
showed that the till examined has a polymineralic composition, typical of Quaternary glacial deposits. All the samples comprise kaolinite, illite and beidellite in the clay fraction, which does not exceed 29% of the total. The dominant mineral is quartz. The goethite share is about 2–3%. The analysis did not show an organic matter content, which was supported by a peroxide oxidation test (according to Polish Standard PN-88/B-04481). The results of granulometric and mineralogical composition measurements are given in Figures 3 and 4.

For the purpose of this study, the glacial till selected was used as an average, model clay soil, the granulometric and mineralogical type of which is widespread in Poland.

The till porosity was studied after its pore medium was:
— ground water
— petrol
— diesel oil.

Selected physical characteristics of the liquids considered are given in Table 1.

The soil material was prepared for porosimetry measurements in three variants:
— undisturbed samples;
— undisturbed samples, air-dried, then saturated with petrol;
— undisturbed samples air-dried, then saturated with diesel oil.

41 porosimetry analyses were performed — on five till samples (G 1 to G 5) for each variant, analysis was replicated 2–3 times.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Distilled water</th>
<th>Petrol</th>
<th>Diesel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [Mg/m³]</td>
<td>1.00</td>
<td>0.74</td>
<td>0.83</td>
</tr>
<tr>
<td>Dynamic viscosity [cP] at 30°C</td>
<td>0.89</td>
<td>0.36–0.49</td>
<td>1.16–3.90</td>
</tr>
<tr>
<td>Water solubility [mg/dm³]</td>
<td>—</td>
<td>131–185</td>
<td>3</td>
</tr>
<tr>
<td>Dielectric constant [-]</td>
<td>78.3</td>
<td>1.9–2.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>

All parameters of distilled water at 25°C; measured by author at ~22°C

To contaminate the soil with petroleum liquids, a free-swell test, introduced by Stomatopoulos and Kotzias (1987), was adapted. It is a simple laboratory experiment, which was proposed by these authors to determine the swelling potential of undisturbed air-dried clays. Firstly, trimmed as needed, an undisturbed soil sample was air-dried. Then, it was placed on a porous rock which was in contact with petrol and diesel oil respectively. The sample and the rock were separated with a filter paper. On the basis of literature data concerning clay mineral-organic interactions (Theng, 1974), it was decided to continue the saturation for about 5 weeks. Due to the chemical aggressiveness of petroleum compounds, the saturation was performed in a glass cylinder, covered with a glass lid to prevent liquid evaporation. The scheme of the assemblage is shown in Figure 5.

According to porosimetry analysis procedure, all samples tested, both natural and laboratory polluted, had to be freed of pore liquid prior to the measurements. This requirement was satisfied by (1) slow air drying, (2) drying in an oven at 60°C. It is believed that for sandy/silty clay soils such drying procedure is acceptable and does not significantly affect soil structure (Frankowski et al., 2001).

The samples were tested using the mercury porosimeter AutoPore IV 9500, Micromeritics, USA. Mercury intrusion porosimetry is a very useful technique to investigate pore space. Not only does it deliver several morphometric characteristics of pore structure, but it also gives many possibilities of data analysis and presentation, including 3D visualisation of...
the pore space. It provides the following sample characteristics:

1. Information that can be deduced directly from intrusion volume and sample mass measurement:
   - total pore volume (mercury intrusion volume) $TIV$ [$cm^3/g$];
   - dry density $\rho_d$ [Mg/m$^3$];
   - particle density $\rho$ [Mg/m$^3$];
   - porosity $\eta$ [%];

2. Information that is obtained by application of the Washburn’s equation (1921):
\[ D = \left( \frac{1}{P} \right) 4 \gamma \cos \varphi \]  

where: \( D \) — pore diameter [\( \text{mm} \)], \( P \) — intrusion pressure [\( \text{MPa} \)]; \( \gamma \) — surface tension [\( \text{dyn/cm} \)]; \( \varphi \) — contact angle between mercury and the solid;

— total pore area [\( \text{m}^2/\text{g} \)];
— median pore diameter — volume [\( \mu \text{m} \)];
— median pore diameter — area [\( \mu \text{m} \)];
— average pore diameter [\( \mu \text{m} \)].

3. Information that is obtained by the application of other theoretical models:
— intrinsic permeability \( k_p \) [\( \text{mD} \)];
— pore tortuosity [-];
— fractal dimension [-].

For detailed information on the general technique of mercury porosimetry and related theoretical models see e.g., Diamond (1970), Griffiths and Joshi (1989) and Webb (2001). A typical report of mercury intrusion analysis is given in Figure 6.

Porosimetry measurements were carried out under a mercury intrusion pressure range of 0.0007 to 206.84 MPa, which corresponds to a pore radius of 400 to 0.006 mm. According to Pazdro and Kozerski’s (1990) classification, this range pertains to the total porosity. However, it is worth noticing that with penetrating open pores only, mercury intrusion does not exactly refer to the total pore volume and should be rather correlated with the open porosity, according to Kleczikowski and Różkowski (2002) terminology.

RESULTS AND DISCUSSION

The detailed results of porosimetry analysis are given in Figure 7. Presumably, the till grain size inhomogeneity is responsible for the variation of values obtained. Even though the tendency of changes due to soil pollution was not always perfectly consistent for all samples, the following facts were determined:

— a reduction in the porosity of samples polluted with petrol and diesel oil. The average porosity value of natural samples (G NS) decreased from 21.4 to 20.4% for petrol-contaminated samples (G B) and to 18.8% for oil-contaminated samples (G ON);
— however, if one compares the effective porosity values, they appear almost identical for all types of sample. G NS: 17.6%; G B: 17.1%; G ON: 17.1%. The effective porosity refers to pores of diameter \( d > 0.2 \mu \text{m} \) (Pazdro and Kozerski, 1990) and was calculated according to the equation:

\[ n_e = \frac{TIV \times \rho_d}{100} \times 100\% \]  

where: \( n_e \) — effective porosity [%]; \( TIV \) — total pore volume for pores of \( d > 0.2 \mu \text{m} \) determined from a pore size distribution curve (Fig. 6B) [\( \text{cm}^3/\text{g} \)]; \( \rho_d \) — dry density [\( \text{Mg}/\text{m}^3 \)];

— the polluted samples show lower values of the total pore volume and the total pore area in comparison with the natural ones. The average values are: G NS: 0.112 cm\(^3\)/g; G B: 0.106 cm\(^3\)/g; G ON: 0.092 cm\(^3\)/g and G NS: 4.11 m\(^3\)/g; G B: 3.53 m\(^3\)/g; G ON: 1.33 m\(^3\)/g respectively;
— the average pore diameter has adversely changed. Its values decreased in the sequence:

G ON: 0.43 \( \mu \text{m} > G \text{ B: } 0.13 \mu \text{m} > G \text{ NS: } 0.11 \mu \text{m} ;
— the dry density values are highest for oil-contaminated samples — G ON: 2.05 Mg/m\(^3\); while the average values of natural and petrol-contaminated soil are quite similar: G B: 1.92 Mg/m\(^3\); G NS: 1.94 Mg/m\(^3\);
— intrinsic permeability and tortuosity values were considerably scattered regardless of the sample type. No clear tendency can be observed here. The permeability ranged from 2.69 to 300 mD for G NS; 2.17–290 mD for G B and 2.58 to 510 mD for G ON samples. The tortuosity ranged from 3.22 to 36 [-] for G NS; 3.74 to 36 [-] for G B and 1.59 to 34 [-] for G ON samples. The permeability and the tortuosity are obtained by application of special theoretical models. To determine the soil permeability on the basis of mercury porosimetry measurements, Katz-Thompson expressions (Katz and Thompson, 1986) are applied. Then, the tortuosity is calculated using permeability data. Obviously, despite the material diversity, this may additionally contribute to experimental error.

Mercury porosimetry analysis revealed several changes in pore space characteristics of the clay soil polluted by petroleum liquids. These changes, however, seem to be an effect of hydrocarbon adsorption onto the soil particles, rather than one of structure rearrangement. Retention of pollutant on the solid phase led to diminution of soil porosity and probably clogging of the smallest pores. Figure 8 provides a good illustration of this. Comparing the pore size distribution of all three types of samples one can realise that the smaller the pore size, the higher the pore volume reduction. Diesel oil affected the soil characteristics more than did petrol, which might be explained by their chemical composition. Diesel oil consists of hydrocarbons with longer carbon chains \( \text{C}_{26} - \text{C}_{29} \), while petrol hydrocarbons contain \( \text{C}_{4} - \text{C}_{10} \) carbon atoms. Bigger molecules are better adsorbed onto the solids due to van der Waals forces. Yet non-polar organic compounds are incapable of breaking strong chemical bonds and electrostatic attraction forces which occur in dry soil, so they failed to truly influence the soil structure.

Intrinsic permeability is related to hydraulic conductivity according to equation (3) (Pazdro and Kozerski, 1990):

\[ k = k_p \frac{g \times \rho}{\eta} \]  

where: \( k \) — hydraulic conductivity [\( \text{m/s} \)]; \( k_p \) — intrinsic permeability [\( \text{mD} \)]; \( g \) — gravity [\( \text{m/s}^2 \)]; \( \rho \) — pore fluid density [\( \text{Mg}/\text{m}^3 \)]; \( \eta \) — pore fluid dynamic viscosity [\( \text{P} \)].

Substitution of average values of \( k_p \) and liquid parameters (as given in Table 1) into equation [3] yields:

— \( k \) of natural till for water is \( 1.28 \times 10^{-6} \text{ m/s} \);
— \( k \) of petrol-contaminated till for petrol is \( 1.67 \times 10^{-6} \text{ m/s} \);
— \( k \) of diesel oil-contaminated till for diesel oil is \( 7.93 \times 10^{-7} \text{ m/s} \).

As for the till samples examined fluid-solid interaction did not bring out significant fabric changes that would be reflected
Fig. 7. The results of mercury porosimetry analysis

Other explanations as in Figure 3
in clear intrinsic permeability changes, the k results obtained seem to depend on the fluids’ fluidity only.

Retention of contaminant on soil particles resulted in reduction in total porosity, total pore volume and pore area; increase in average pore diameter and dry density, but no substantial pore space changes have been observed. Similar conclusions were reached by Berger, Kalbe and Goebbel (2002). They stated that a 12-year long influence of organic compounds did not cause significant changes in the fabric of silty clay liner material. The authors attributed their findings to low pollutant concentration.

Oppositive results, however, are also reported in the literature. Examination of samples permeated with organic liquids revealed formation of cracks in the soil. (Anandarajah, 2003). Korzeniowska-Rejmer (1997, 2001) observed voids under building foundations in soil, which had been polluted with oil substances for about 50 years. SEM (scanning electron microscopy) images of silt from this area identified qualitative alteration of its microstructure.

CONCLUSIONS

In this study quantitative analysis of glacial till pore space was performed using the mercury porosimetry technique. Natural soil and samples polluted in the laboratory with non-polar organic liquids were tested. The soil material had been air-dried before it was exposed to the pollutant. For the test conditions as defined, the analysis did not reveal any evidence of substantial structural rearrangement of the soil. Pore space characteristics changed, however, due to adsorption of hydrocarbon molecules onto the solid phase. This resulted in:

— reduction in total pore area, total pore volume and porosity;
— increase in average pore diameter and dry density.

The results obtained suggest that in the short term, non-polar organic compounds are incapable of breaking strong chemical bonds and electrostatic attraction forces that occur in dry soil so as to alter its microstructure. It should be underlined that the conclusions do not directly carry over to water-saturated soils. In the latter case organic migration and interaction with the solid phase are heavily influenced by the presence of water in pore spaces.

In the light of the findings presented and literature data, the question of the influence of non-polar organic on clay soil structure and permeability does not admit of a straightforward answer and needs further investigation.

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REFERENCES


POLISH STANDARD PN-88/B-04481 — Grunty budowlane. Badania próbek gruntu.


