1	Determination of Residual Concentration of Active Polymer in a
2	Polymeric Support Fluid
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### 1 Abstract

2 This paper is concerned with the properties of synthetic polymer fluids used for the temporary 3 support of excavations such as pile bores and diaphragm wall panels. These fluids can be used 4 as alternatives to bentonite slurries and may influence the performance of the foundation 5 elements formed under them. During the excavation process polymers tend to be sorbed onto the 6 soil and they also may be degraded by the shearing in pumps etc. It follows that a controlling 7 parameter for these fluids is the residual concentration of active polymer in the fluid and this 8 paper considers test methods that may be used for its determination. Three different measuring 9 principles, namely total organic carbon, UV light absorption and viscosity, were investigated for 10 their suitability for site use. Their performance was compared in a series of polymer-clay 11 sorption experiments – the clay sorbing the polymer and so reducing the residual concentration 12 in solution. A method based on the measurement of viscosity of centrifuge supernates was found 13 to have the best overall performance. A comparison with current assessment criteria based on 14 Marsh funnel viscosity and density measurements confirmed the superiority of the proposed 15 method for detecting polymer loss by sorption. Further evaluations showed that the proposed 16 method is not limited to any specific combinations of polymers and soils. The proposed method 17 will allow site engineers to have greater control over the properties of the fluids on site. 18 [232 words]

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20 Keywords: Excavation; Organic carbon; Polymer concentration; Slurries; Sorption; Viscosity.

### 1 Introduction

2 Synthetic polymer fluids have been in regular use for the construction of deep foundations in 3 many parts of the world since the early 1990s. These are molecularly engineered fluids which 4 can be used in place of conventional bentonite slurries as the support fluids for excavations such 5 as pile bores and diaphragm wall panels. Although both polymer fluids and bentonite slurries act 6 by exerting a hydrostatic pressure on the side walls of an excavation to maintain its stability, they 7 are very different in their composition and behaviour. Bentonite slurries are dilute suspensions 8 of the sodium montmorillonite clay in water, and concentrations are typically between 2.5 and 9 5 wt% corresponding to a fluid density range of between 1.014 and 1.028 g/cm<sup>3</sup>. In contrast 10 synthetic polymers dissolve into the mix water and the concentrations used are typically in the 11 range of 0.05 to 0.2 wt% (Jefferis et al. 2011). Due to the very low dosage, the density of a clean 12 polymer fluid is effectively that of water.

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14 Clay slurries develop their rheological properties by interactions between the suspended colloidal 15 clay particles but the mechanism by which polymer fluids generate their viscosity is very 16 different. The polymers used in excavation fluids have very high molecular weights, typically 17 between 12 and 17 million g/mol (O'Neill and Reese 1999) and could measure up to 60 µm 18 along their long-chain backbones. The molecules also can have functional side groups carrying 19 ionic charges. When dissolved in water the polymer molecules continually interact with each 20 other through hydrodynamic and electrostatic forces to produce a solution of high viscosity. 21 Figure 1(a) shows a schematic diagram to illustrate the molecular interactions in a polymer fluid. 22 The polymer molecules can bind to soil particles and inhibit the break-up of lumps of cut soil 23 and the dispersion of fine soils into the fluid but as a result they are removed from solution and 1 so the active concentration is reduced.

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3 Since the viscosity of a polymer fluid is the result of molecular interactions, it is sensitive to 4 external influences. These include contaminants from the ground (Majano et al. 1994), high 5 shear induced by pumping equipment (Lam et al. 2010a) and physical/chemical interactions with 6 the in-situ and cut soil particles whilst in use (Jefferis and Lam 2013). The last effect, although 7 perhaps the most significant in the field, is the least reported and so there is very little 8 information about it in the geotechnical literature. This paper bridges this knowledge gap by first 9 presenting a discussion on the effect of soil sorption, and then the development of a test method 10 which can be used to measure the residual (active) polymer concentration in used fluids.

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## 12 **Polymer Sorption and the Effect of "Flipping"**

13 Because the effect of polymer-soil interactions in a polymer-supported excavation is still poorly 14 understood, it tends to be ignored in the field. Therefore, it is not uncommon to find polymer 15 fluids, after repeated reuse, containing large amounts of suspended soil but potentially little or no 16 residual polymer in solution. This occurs because the action of the digging tools will bring in-17 situ soils into suspension in the fluid. Large particles will settle relatively fast, but those smaller 18 than coarse silt will tend to remain in the fluid for much longer due to the high fluid viscosity 19 and the consequently low settling rate of fine particles. In addition to their physical effects on 20 the fluid properties, the soil surfaces, especially those of clays, provide sites onto which polymer 21 molecules can sorb. This phenomenon is known as polymer sorption and may be promoted by 22 charged functional groups on the polymer chains. The ability of the polymer molecules to bond 23 to soil particles is actually a very important feature of polymer fluids, as it allows the molecules

1 to interact with the soil at the side walls of an excavation and so reduce the amount of swelling in 2 clay soils or slaking in argillaceous rocks (e.g. Likos et al. 2005; Invang et al. 2007; Brown and 3 Axtell 2010). Because there is no filter cake formed during the process, the interface shear 4 strength between the soil and the completed foundation element does not appear to be affected as 5 shown by previous studies (e.g. Ata and O'Neill 2000; Lam et al. 2010b). In addition to the 6 coating effect on side wall, the polymer molecules can also encapsulate the cut soil as lumps and 7 prevent it from disintegrating into smaller pieces (Jefferis et al. 2011). As a result, the cut soil 8 can fall out of suspension more rapidly so that the polymer fluids can remain relatively free of 9 suspended soil. Figure 1(b) shows a schematic of the behaviour of a working polymer fluid in an 10 excavation in a fine-grained (clay and silt) soil.

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12 A common misconception among field operatives is that once the polymer fluid has been mixed 13 it will continue to function properly, or possibly improve due to the accumulation of soil 14 particles in suspension, i.e., becoming more like a slurry. This is a dangerous fallacy. Since 15 sorption of polymers onto soils removes them from solution, the soil-binding and side-wall 16 coating abilities can be lost if the suspended soil particles are not removed and the fluid not 17 reconditioned by addition of fresh polymer after use (KB Technologies 2002). Maintenance of 18 fluid properties can be achieved by the use of simple sedimentation tanks coupled with regular 19 addition of sufficient new polymer materials to maintain fluid properties and also to ensure that 20 the cut soil remains as rapid settling lumps and does not disperse into the slurry – hence the 21 importance of measurement of the residual polymer concentration. If these steps are not taken, 22 the end result will be a water-native soil mixture which has no active polymer left in the system 23 (i.e. no free polymer to develop solution properties including bonding to soil particles). This

1 kind of exhausted polymer fluids is referred to as a "flipped" system in this paper. Reversing a 2 flipped system is very expensive in polymer usage as once the fluid has flipped, the soil cuttings 3 will disperse and require very much more polymer to satisfy their exposed surface bonding sites 4 than would have been required to maintain them as coarser lumps (KB Technologies 2002). The 5 best strategy is therefore to keep ahead of polymer demand but currently there are no established 6 methods to determine the residual polymer concentration and hence to assess the risk of flipping. 7 The consequences of allowing a polymer fluid to flip are that all the functional effects of the 8 polymer are lost. As a result, the slurries will require considerably more effort and equipment for 9 spoil removal, swelling and sloughing of side walls in water-sensitive formations are not 10 inhibited, and a soft native soil filter cake may form in permeable soils. Figure 1(c) depicts the 11 situation where a polymer fluid has flipped. Figure 2 shows photographs of a clean fluid and one 12 which has flipped.

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14 The lack of a procedure for the determination of residual polymer concentration is most 15 unfortunate as there are many undesirable effects associated with flipped polymer fluids which 16 are effectively native soil-water slurries. All the test methods that are currently in use with 17 polymer fluids have been blindly transposed from the existing practice with bentonite slurries: 18 fluid density (ASTM D4380-12), sand content (ASTM D4381 / D4381M-12), and Marsh funnel 19 viscosity (ASTM D6910 / D6910M-09). The origins of these tests can be traced back to the 20 1930s when clay-based slurries became widely used for oil well drilling (Rogers 1948). Direct 21 adoption of these test methods for polymer fluids, rather than the development of polymer-fluid 22 specific tests, has led to great difficulty in specifying quality control procedures for polymer 23 fluids. Suppliers of polymer materials can do no more than recommend operating properties

1 based on the existing test methods – methods which were designed for a completely different 2 type of material, i.e., bentonite. For instance, to avoid the problem of flipping, one supplier 3 suggests that the fluid density should be no higher than 1.015 g/mL and that the minimum Marsh 4 funnel viscosity should be at least 60 seconds. As will be shown later, under certain conditions 5 polymer fluids which have been flipped can still comfortably satisfy these requirements, 6 demonstrating the inadequacy of these test methods and the assessment criteria. Partly due to 7 these problems, a set of industry-approved specifications for synthetic polymer fluids still does 8 not exist after almost two decades of polymer use. For example, O'Neill and Reese (1999) did 9 not specify polymer fluid properties in the drilled shaft manual of the Federal Highway 10 Administration (FHWA) and the latest edition of the ICE Specifications for Piling and 11 Embedded Retaining Walls (Institution of Civil Engineers 2007) does not specify properties for 12 polymer fluids although it does so for bentonite slurries. This situation persists today.

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To address some of these problems a laboratory investigation was undertaken to establish the most suitable method for the determination of residual polymer concentration in the field. In the following sections, a brief introduction to the types of polymer used will be given, which is followed by a review of the available measurement techniques. The experimental data from three selected measurement techniques will then be compared to enable the most suitable one to be assessed.

#### **1** Polymer Types, Selection Criteria and Initial Screening of Test Methods

2 The first stage of the search for a suitable test method was to develop an appreciation of the types 3 of polymers that are currently used. Although the word "polymer" encompasses everything that 4 is composed of molecules with repeating structural units (DNA, plastics, rubber, etc.), in 5 foundation drilling it is often used to refer to a particular class of synthetic polymers known as 6 partially hydrolyzed polyacrylamides (PHPAs) or their derivatives (O'Neill and Reese 1999). 7 PHPAs belong to a family of acrylamide copolymers which have the formula 8  $[-(CH_2CHCONH_2)_x-(CH_2CHCOOH)_y-]_n$ , where the subscripts x and y indicate the proportions 9 of the acrylamide and acrylic acid monomers in each repeating unit and the subscript n indicates 10 the number of repeating units in a polymer molecule. In addition to the base polymers, most 11 suppliers provide a range of proprietary additives to improve the performance of the system. 12 Additives may perform a wide range of functions including fluid loss control, accelerating 13 settlement of suspended soil particles, and weighting of the fluid to enhance excavation stability 14 though in the authors' experience the weighting agents are rarely necessary. Some suppliers 15 provide pre-mixed blended polymers for simpler application on site.

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17 Alongside and prior to their use in geotechnical construction, PHPAs have been used in many 18 other applications including water treatment, oil-well drilling and soil stabilization for surface 19 erosion control. Therefore, the sorption of these molecules onto soil particles has been a subject 20 of interest and research for many years. This has resulted in the development of different 21 methods for the determination of residual polymer concentration after interactions with soil and 22 other particles. Taylor and Nasr-El-Din (1994) summarize seventeen methods, each of which is 23 based on a different measurement technique, ranging from advanced analytical procedures such 1 as electron spin resonance spectroscopy to rather simple ones such as turbidimetry. The methods 2 vary considerably in terms of their accuracy, complexity, requirements for test equipment, etc. 3 Nonetheless, the list of Taylor and Nasr-El-Din was used as the best available starting point in 4 the search for a suitable test method for geotechnical application. To ensure the chosen 5 technique(s) can properly satisfy the needs and the requirements of this industry, the following 6 criteria were identified:

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The measurement technique should work with different polymer chemistries, from the
 basic PHPAs to the more complicated polymer blends. Therefore, it should not rely solely
 on the physical or chemical properties of specific functional groups of the PHPAs such as
 the amide (-CONH<sub>2</sub>) or the carboxylic acid (-COOH) groups;

- For health and safety reasons, the test should not require the use of radioactive or otherwise
   hazardous materials such as concentrated acids;
- The test equipment should be portable and require no more than an electrical supply to 15 function, i.e., there should be no need for special gases, high pressures or vacuum;
- The test procedure including specimen preparation should not be too complex. It should be
   practicable by a trained technician;
- The analysis time should not be too long. A maximum of 30 minutes is considered realistic
   to meet the hectic schedules of typical construction sites; and
- The test result should be relatively tolerant of contaminant species which can enter 21 polymer fluids from the excavated ground.

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23 Applying these criteria to the seventeen methods of Taylor and Nasr-El-Din resulted in the

1 exclusion of all but three of the candidate techniques. These three were based on the principles 2 of: total organic carbon (TOC) content, absorption of ultraviolet light (UV spectroscopy) and 3 fluid viscosity. Thermogravimetric analysis (TGA), which was not on the list of Taylor and 4 Nasr-El-Din but was used successfully by Bae and Inyang (2006), fails to satisfy some of the 5 selection criteria because it requires the use of argon gas and drying in an oven which extends 6 the test time. No other methods have been identified which satisfy all the requirements set out 7 above. To find the most suitable of the three techniques, their performance was assessed in a 8 series of polymer sorption experiments as described below.

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## 10 Experimental Details

#### 11 Materials Used

SlurryShield FGP<sup>5</sup>, which is a polymer blend consisting of modified PHPAs and several other 12 13 chemical additives, was chosen for the sorption experiments as it represents one of the more 14 developed polymer systems currently available in the marketplace. It is supplied in dry powder 15 form and has a creamy white color. Detailed information about the chemical composition of this 16 product is given in Goodhue and Holmes (1997). According to the supplier, the recommended field dosage of this polymer may range from 0.8 to  $2.5 \text{ kg/m}^3$  depending on the expected soil 17 conditions. When used for the experiments, it was prepared at a concentration of  $3 \text{ kg/m}^3$  (0.3) 18 19 wt%) – a high concentration for this material but it was to be diluted 50% by the addition of the 20 clay test slurry. As polymer fluids are shear-sensitive (Lam et al. 2010a), an axial flow impeller 21 mixer rotating at a low speed of 300 r/min was used so as not to apply unnecessary shear to the fluid during mixing. The polymer fluid was prepared a day prior to use to ensure that there were 22

<sup>&</sup>lt;sup>5</sup> SlurryShield® FGP<sup>TM</sup> is a trademarked product of KB International LLP (formerly KB Technologies), Chattanooga, TN.

no time effects regarding dissolution or hydration of the powder but discarded after a week to
avoid any effects of aging – the properties of PHPA polymer can degrade with time but typically
over periods of much more than a week. Natural polymers such as guar and xanthan gum can
degrade rather rapidly unless treated with a preservative.

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A sodium-activated bentonite "SPV 2000"<sup>6</sup> was used as an absorbent in the sorption 6 7 experiments. It was chosen for its well characterized chemical structure and properties (e.g. 8 Kawatra and Ripke 2001; Stewart et al. 2001). Also sodium bentonite, because of its high 9 specific surface area, should represent a worst-case sorption scenario for polymer sorption in the 10 field (note that the best-case scenario in terms of sorption would be drilling in clean coarse sand). 11 The cation exchange capacity of the bentonite was measured using the methylene blue index 12 (MBI) method (ASTM C837-09) as 79 meq/100 g, equating to 79% montmorillonite content 13 assuming an MBI for pure montmorillonite of 100 meg/100 g. The bentonite powder was mixed 14 with deionized water to form clay slurries with a range of concentrations up to  $100 \text{ kg/m}^3$ . In 15 contrast to the polymer fluids, bentonite slurries require high-speed mixing for full development 16 of their properties (Jefferis 1982) so these slurries were mixed at a rotational speed of 17 6000 r/min. The slurries were also prepared a day before use to allow some time for hydration of 18 the clay particles.

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## 20 Preparation of Test Specimens

21 The clay slurries were added to the polymer fluids at a 1:1 volume ratio to form a series of 22 mixtures with a polymer concentration  $(c_p)$  of 1.5 kg/m<sup>3</sup> and clay concentrations  $(c_c)$  ranging

<sup>&</sup>lt;sup>6</sup> SPV 200 is supplied by CETCO Europe Ltd. (formerly Volclay), England, United Kingdom.

from 0 to 50 kg/m<sup>3</sup>. The resulting density ( $\rho_{\rm f}$ ) at 20°C of these mixtures ranged from 0.998 to 1 1.025 g/cm<sup>3</sup>, replicating a perfectly clean fluid at the beginning of an excavation to a heavily 2 3 clay-laden fluid after repeated reuse. The polymer fluid and clay slurry were mixed at a low 4 speed until a uniform consistency was achieved. They were then placed on an orbital shaker for 5 at least 24 h to ensure effectively full sorption. The clay particles were then removed from the 6 mixtures by centrifugation prior to polymer concentration determinations on the supernate, i.e. 7 the clear liquid. With the authors' micro-centrifuge it required about 15 min to produce a supernate of reasonable transparency with trivial clay content. For each specimen, a total of 8 9 20 mL of supernate was needed to run the three selected test procedures. Prior removal of the 10 suspended soil particles from the fluid was a necessary step for each of the three concentration 11 measurement techniques.

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#### 13 Test Methods for Polymer Concentration Measurements

# 14 The principles and operations of the three measurement methods, i.e., TOC content, UV 15 spectroscopy and viscosity, are discussed below.

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17 TOC content ( $c_{\text{TOC}}$ ) has been commonly used to measure polymer concentrations in the field of 18 oil and gas exploration (Lecourtier et al. 1990; Bailey et al. 1994; Levy and Miller 1999). The 19 technique works by determining the organic carbon content of the fluid and requires an 20 assumption that all the carbon is derived from the polymers, i.e., from the carbon chain 21 backbones and any pendant groups. The determined TOC includes all carbon compounds except 22 inorganic carbon such as carbonates. A calibration curve for the clean polymer fluid was 23 constructed using a TOC analyzer (model TOC-V<sub>CSH</sub>, Shimadzu Corp., Japan – note that this is a

1 laboratory-based model but portable versions are also available). Figure 3 shows the test results 2 and a linear trend line fitted through the averages at each concentration. As can be seen, the 3 trendline does not fit the data points well, and the differences between repeated measurements 4 are rather large for the specimens with high concentrations. This is believed to be caused by the 5 high viscosity of the fluid which could have affected the fluid volume (typically 10 to 2000  $\mu$ L) 6 injected into the oxidation chamber. It may be noted that for a polymer containing only PHPAs the theoretical TOC content in  $kg/m^3$  should be around 50% of the concentration of the polymer, 7 8 i.e., the polymer concentration should be twice the TOC. However, for the test polymer the best 9 fit line to the data showed only about 30% thus confirming that it is not solely formed from 10 PHPAs.

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12 The UV spectroscopy method has been used by Beazley (1985) and Deng et al. (2006) to 13 measure polymer concentration. It is an optical method which relies on the absorption of light in 14 the far UV range between 190 and 400 nm. The measured absorption can be related to 15 concentration via the Beer-Lambert law:  $A = \varepsilon lc$  where A is the absorbance,  $\varepsilon$  is the absorption 16 coefficient, l is the length of the light path and c is the concentration of the absorbing species, 17 i.e., the polymers. This relation was investigated for the chosen polymer and Fig. 4 shows a 18 series of calibration curves for wavelengths between 190 and 215 nm. The variation between 19 repeated measurements was very small (standard error of mean typically less than 0.004) and 20 hence errors bands are not displayed on the figure. The measurements were made with a UV-21 visible spectrophotometer (model Helios Gamma, Thermo Fisher Scientific, England) equipped 22 with a far-UV quartz cell with a path length of 1 cm. It can be seen that the Beer-Lambert linear 23 relationship between absorbance and concentration was satisfied at all wavelengths but at the expense of a 20-times dilution of the polymer specimens as at high concentration non-linearity
 was found to occur. Investigation of the absorption data showed that the polymer concentration
 was most sensitive to light wavelengths of 190 and 195 nm and therefore only these wavelengths
 were used.

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6 The viscosity method has been also used for polymer concentration measurements by researchers 7 including Mungan (1969), Jungreis (1981) and Inyang et al. (2007). This method takes 8 advantage of the fact that viscosity  $(\eta)$  is the manifestation of the hydrodynamic interaction 9 between the charged polymer molecules in solution (Fig. 1a). The amount of active (viscosity 10 generating) polymer remaining in the system is obtained simply by measuring the viscosity of 11 the suspended solids-free supernate and converting it to a concentration via calibration curve(s). 12 The viscosity measurements were undertaken with a Brookfield viscometer (model DV-II+, 13 Brookfield Engineering Laboratories, Mass.) equipped with a UL (ultra-low) adaptor as were the 14 associated calibration curves which are shown in Fig. 5. For the viscosity measurements, about 15 16 mL of the centrifuge supernate was filled into the UL adaptor; the spindle then inserted into 16 the fluid column and connected to the viscometer head. The UL adaptor was connected to a 17 water bath for control of the specimen temperature. Further information on the viscometer is 18 given in the manufacturer's literature (Brookfield Engineering 2005) and ASTM D4016-08 19 which describes its use for analyzing chemical grouts for application in soil and rock. 20 Advantages of this equipment setup are that it can accurately determine viscosities as low as that 21 of water (1 mPa·s) whereas many other portable viscometers are unable to achieve this and that it 22 requires only 16 mL of test fluid for measurements which can be a real advantage in terms of 23 reducing centrifugation time on site. The curves given in Fig. 5 were constructed for spindle

speeds ranging from 0.5 to 5 r/min at a reference temperature of 23°C. Repeated measurements yielded error bars smaller than the symbol size and so these are not shown in the figure. The use of multiple calibration curves was not necessary but helped to assess the sensitivity of the result to the choice of spindle speed.

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### 6 Marsh Funnel Viscosity of Polymer-Clay Mixture

7 In addition to the three selected test procedures, a series of tests was undertaken with a Marsh 8 funnel to investigate whether this field test coupled with fluid density measurement could act as 9 an alternative to the laboratory procedures. For this test work, the viscosity of the polymer-clay 10 mixtures was measured with a Marsh funnel (ASTM D6910 / D6910M-09) to investigate the 11 adequacy of this method for determining the degree of polymer sorption. The test involves 12 filling the funnel with 1.5 L of test fluid and measuring the efflux time for 946 mL (one U.S. 13 quart) to flow out from its tip. The results are reported as the Marsh funnel viscosity in seconds. 14 Note that this method is only a crude indicator of relative viscosity as it involves a flow time 15 measurement, as opposed to the viscometer which measures apparent viscosity as the ratio of 16 shear stress ( $\tau$ ) to shear rate ( $\dot{\gamma}$ ).

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#### 18 **Evaluation of Test Methods**

#### 19 Comparisons between TOC, UV and Viscosity Methods

The residual polymer concentration  $(c_p)$  in each sorption specimens as measured by the three methods are given in Figs. 6 to 8. For each of the plots, the error bars represent the standard errors and the mean values have been fitted with an exponential function. As expected, the three figures all show a decreasing trend of residual polymer concentration as the clay concentration (c<sub>c</sub>) increases, although there is clear difference in the apparent rate of reduction between them.
It is interesting to see that in none of the plots the residual polymer concentration approaches
zero at high clay concentrations, suggesting that some of the materials in the polymer blend do
not adsorb onto the clay. This can be explained by the presence of different polymer species in
the blend each with its own degree of soil affinity.

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7 In terms of individual performance, the TOC method seems to be the least repeatable as shown 8 by the large errors between repeated measurements and the low R-squared value of the fitted 9 equation (Fig. 6). As previously stated, this poor performance is believed to be due to the high 10 viscosity of the test fluid which may have caused variations in the injected volume. In contrast 11 the UV spectroscopy results have much better repeatability, but at higher clay concentrations 12  $(c_c)$  the degree of scattering becomes larger (Fig. 7). This is believed to be due to remnant 13 ultrafine clay particles (<0.05  $\mu$  m) present in the supernate – such fines can absorb light and 14 therefore interfere with the results. Increasing the centrifugation time might solve this problem 15 but an increased time could render the method unsuitable for use on site where test schedules are 16 tight. The viscosity method does not suffer from this problem, as a trace amount of clay will 17 have a negligible effect on the viscosity (Fig. 8). The viscosity method has also demonstrated 18 superiority in a few other areas. For example, the results from the viscosity method show a more stable plateau ( $c_p \approx 0.62 \text{ kg/m}^3$ ) at high clay concentrations than the other methods. The R-19 20 squared value for the viscosity technique was also the highest (0.98) of the three methods. 21 Finally, it should also be noted that the results obtained from calibration curves derived at 22 different spindle speeds were found to be similarly consistent (as shown by the small error bars

on the plot). This indicates that the choice of viscometer speed is not important as long as the
 induced torque can be accurately measured, i.e., the signal-to-noise ratio is not too low.

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4 Based on the results of these trials, the viscosity method appears to provide the best performance 5 of the three. It is well suited to use on site as the viscometer is portable and requires only 6 electrical supply to function. Other benefits include simple specimen preparation (e.g. no 7 dilution) and short measurement time (10 to 15 s for each measurement). Furthermore, as most 8 slurry technicians are already familiar with the concept of viscosity, at least in a general sense, 9 this method should be easy for them to assimilate. This aspect of site testing is very important 10 and should not be overlooked. Tests based on complex measurement principles are unlikely to 11 be well received on site and spurious errors may be introduced.

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#### 13 Further Considerations regarding the Viscosity Method

14 To complete the assessment of the viscosity method, a further literature review was carried out to 15 compare the accuracy of this method with the more sophisticated laboratory-based techniques. It 16 was found that a comparison has been made by Bae and Inyang (2006) who concluded that TGA 17 provides a more accurate determination of the actual quantity of polymer molecules sorbed onto 18 clay particles. This is because the freeze-drying preparation process used for the TGA can 19 release those polymer molecules which are simply trapped between the soil particles (Fig. 1), so 20 that only those which are actually sorbed are measured by this method. However, this feature is 21 not relevant to foundation drilling as the key concern is the amount of useable polymer left in the 22 fluid, i.e., the polymer available for bonding with newly exposed soil particles and developing 23 solution properties, rather than the amount of polymer that has been sorbed. For this reason,

polymer molecules which are trapped should be counted as if they have been sorbed and hence
 the results obtained from the viscosity method should be the most useful for the application
 concerned.

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## 5 Evaluation of Current Approach to Limiting Polymer Sorption

As mentioned before, the Marsh funnel viscosity ( $\eta_{\rm MF}$ ) and fluid density ( $\rho_{\rm f}$ ) are currently used 6 7 as indirect indicators of polymer sorption in the field since no other methods are available. To 8 evaluate the adequacy of this approach, the  $\eta_{\rm MF}$  and  $ho_{\rm f}$  of the polymer-clay mixtures prepared for the previous comparison were determined. Figure 9 shows  $\eta_{\rm MF}$  plotted against  $c_{\rm c}$  (top) and 9  $\rho_{\rm f}$  (bottom) with the area outside the current acceptable limits shaded. It is interesting to see 10 that  $\eta_{\rm MF}$  reached a minimum of 87 s at  $c_{\rm c}$  of  $10\pm5~{\rm kg/m^3}$  and then it followed an upward trend 11 to reach 100 s at 50 kg/m<sup>3</sup>. This phenomenon is thought to be due to the clay particles initially 12 13 reducing the hydrodynamic volumes of the polymer molecules due to charge neutralization and 14 therefore reducing the fluid viscosity. As  $c_{\rm c}$  continued to increase, the clay particles became the dominant species and therefore increase the viscosity. If this change is assumed to occur at  $c_c$  of 15 10 kg/m<sup>3</sup>, then according to Fig. 8 the corresponding  $c_p$  was about 0.9 kg/m<sup>3</sup>, at which stage 16 about 68% of the active polymer content [total (1.5 kg/m<sup>3</sup>) minus inert (0.62 kg/m<sup>3</sup>)] had been 17 18 sorbed. This means that suspended soils became rheologically dominant well before all the 19 active polymers were removed from solution. This shows that the viscosity of a polymer-clay 20 mixture is not a good indicator of the amount of active polymer left and that the only way to 21 measure polymer sorption is by analyzing the properties of the supernate as described in the 22 earlier sections.

Figures 8 and 9 together also allow the current fluid specifications, which are based on Marsh funnel and density measurements, to be evaluated. It can be seen that the test fluid had lost most of its active polymers well before it reached a fluid density of 1.015 g/cm<sup>3</sup> – an upper limit density suggested by one polymer supplier to prevent fluid flipping (KB International 2007). Furthermore, the Marsh funnel viscosity never dropped below the typical lower limit of 60 s. These findings again show the inadequacy of using the Marsh funnel viscosity and density of solid-laden fluids as indicators of polymer sorption.

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## 10 Further Evaluation of the Proposed Method

11 As the previous comparison was made using one particular polymer-soil combination, to confirm 12 the usefulness of the viscosity method for other systems another series of tests was carried out. The polymer used was a PHPA called "Shore Pac"<sup>7</sup> which is specifically marketed for 13 14 foundation drilling by CETCO. The molecular weight and the degree of hydrolysis of this 15 polymer have been determined as 22 million g/mol and 39% respectively (Lam 2011). According to the supplier, the recommended dosage of this polymer ranges from  $0.4 \text{ kg/m}^3$  for 16 clay to 1.2 kg/m<sup>3</sup> for coarse gravel. A dosage of 0.4 kg/m<sup>3</sup> was used for the tests. The soil used 17 was London Clay taken from a central London site. The MBI of this soil is 21 meq/100 g, which 18 19 is considerably lower than that of the sodium bentonite. The specimen preparation and test 20 procedures were the exactly same as the previous series of tests.

<sup>&</sup>lt;sup>7</sup> Shore Pac® is a product of CETCO Drilling Products, IL.

1 Figure 10 shows the test results. Note that the scale of the plot is smaller than the previous ones 2 due to the lower initial polymer concentration. It can be seen that, although the polymer 3 reduction pattern resembles those of the previous tests, the fitted plateau value is much lower at  $0.03 \text{ kg/m}^3$  and approaching a negligible value. This is because the polymer used is not a 4 5 blended product but a PHPA and hence all the polymer molecules, except the impurities, should 6 be reactive to the clay particles. Therefore, at high clay concentrations the residual polymer 7 concentration is close to zero. It can also be seen that the degree of repeatability (as shown by 8 the error bars) and curve fitness (as shown by the R-squared value) are again very good. This 9 confirms that the performance of the proposed method is not limited to any specific 10 combinations of polymers and soils.

11

12 Finally, to aid the comparison between this and the last series of tests, the sorption isotherms 13 have been produced and are given in Fig. 11. The amount of polymer sorption, A, expressed as 14 the amount of polymer sorbed per unit weight of soils (kg/kg) is plotted against the equilibrium (residual) polymer concentration,  $c_{\rm p}$  (kg/m<sup>3</sup>). It can be seen that the rate of sorption, as shown 15 16 by the initial gradients of plots are rather similar for the two systems. However, the final plateau 17 value of the bentonite system is about twice that of the London Clay. This is because bentonite 18 has many more available sorption sites than the London Clay and hence the amount of maximum 19 sorption is higher.

20

## 21 Conclusions

A test method based on viscosity measurement of centrifuge supernates has been proposed foruse with polymer support fluids. In contrast to the existing method which requires a combination

1 of Marsh funnel and density measurements, the proposed method allows residual polymer 2 concentrations in used fluids to be directly determined. This method has been checked against a 3 list of requirements to ensure its suitability for use on site and it compared favorably with two 4 other measurement techniques in a series of polymer-soil sorption experiments. Further checks 5 were carried out using another polymer-soil system and the same consistent performance was 6 found. Viscosity-concentration calibration curves for a particular commercial polymer product 7 have been determined as part of this research. For other polymer products the necessary 8 calibration curves can be constructed by testing fluids over a range of known polymer 9 concentrations.

10

11 The test method presented in this paper will allow foundation contractors and consulting 12 engineers to have greater control over and supervision of the properties of polymer support 13 fluids. Ultimately, it is hoped that the test method will allow polymer suppliers and industry and 14 client groups to develop a set of performance specifications based on tests that are truly suitable 15 for polymer fluids.

16

#### 17 Acknowledgments

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# 1 Appendix

2	То а	id deployment of the proposed method, a step-by-step procedure for use by site personnel is
3	set o	but below and an example of the complete instrument setup is shown in Fig. A1.
4		
5	1.	Prior to the site testing, prepare viscosity calibration curves. For the calibration, it may be
6		useful to adopt a temperature slightly above that expected on site in hot weather so that
7		only heating and not cooling, which can require refrigeration equipment, is required on
8		site;
9	2.	Sample the test fluid from the shaft, trench or settlement tank;
10	3.	If the fluid contains a significant amount of suspended solids, allow the sample to stand for
11		1 to 2 min to allow the coarsest particles to settle;
12	4.	Centrifuge about 25 mL of the fluid using a micro-centrifuge at an acceleration of 15,000 g
13		or more to obtain at least 16 mL of supernate. This process should take no more than about
14		15 min;
15	5.	Transfer the supernate to the UL adaptor of the Brookfield viscometer and assemble the
16		adaptor unit to the viscometer head;
17	6.	Prepare the water bath at the temperature at which the calibration curves were constructed.
18		If the water bath is equipped with a built-in circulatory pump, connect the pump to the UL
19		adaptor. If a pump is not available, simply immerse the adaptor into the water bath. In
20		either case, allow 1 to 2 min for the specimen temperature to equilibrate. If a water bath is
21		not available use a wide mouthed vacuum flask with water temperature adjusted to that
22		required for test;

1	7.	Measure the viscosity at the rotational speed(s) for which the calibration curve(s) were
2		constructed. For best signal-to-noise ratios with low viscosity specimens, make
3		measurements at the highest speed for which a calibration curve is available. Similarly,
4		make measurements at a low speed for high viscosity specimens to avoid the measured
5		torque exceeding the instrument limit;
6	8.	Read off the corresponding polymer concentration from the calibration curve for the
7		chosen viscometer speed;
8	9.	For improved confidence in the result repeat steps 7 and 8 at a second speed.
9		

10 The test procedure described above (excluding step 1 – fluid sampling) should take less than
30 min to complete by a trained field technician.

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1	List of Footnotes	
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3	1.	1st author byline
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5	2.	2nd author byline
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7	3.	3rd author byline
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9	4.	4th author byline
10		
11	5.	SlurryShield® FGP <sup>TM</sup> is a trademarked product of KB International LLP (formerly KB
12		Technologies), Chattanooga, TN.
13		
14	6.	SPV 200 is supplied by CETCO Europe Ltd. (formerly Volclay), England, United
15		Kingdom.
16		
17	7.	Shore Pac® is a product of CETCO Drilling Products, IL.



Schematic diagrams showing the various conditions of polymer support fluids: a) clean, b) working condition and c) completely exhausted 171x111mm (300 x 300 DPI)

 $\begin{array}{r} 47\\ 48\\ 49\\ 50\\ 51\\ 52\\ 53\\ 54\\ 55\\ 56\\ 57\\ 58\\ 59\\ 60\\ \end{array}$ 



(a)



(b)

Photographs of polymer support fluids: a) clean and b) completely exhausted 42x71mm (300 x 300 DPI)



Calibration curve for the TOC method 60x42mm (300 x 300 DPI)



Calibration curves for the UV spectroscopy method 60x42mm (300 x 300 DPI)







Polymer sorption results by the TOC method 60x43mm (300 x 300 DPI)



Polymer sorption results by the UV spectroscopy method 60x43mm (300 x 300 DPI)



Polymer sorption results by the viscosity method 60x43mm (300 x 300 DPI)



Marsh funnel viscosity of polymer-clay mixtures 60x42mm (300 x 300 DPI)



Polymer sorption results of a PHPA-London Clay system measured by the viscosity method 60x42mm (300 x 300 DPI)





Sorption isotherms of the two investigated polymer-soil systems 61x44mm (300 x 300 DPI)



Equipment setup for the proposed viscosity method 85x63mm (300 x 300 DPI)