Project Title: "WET SOLIDS FLOW ENHANCEMENT"

Semi-Annual Report
DOE Award Number: DE-FG22-95PC95219

Department of Chemical Engineering and Department of Chemistry
Lehigh University
Grant Date: 7/10/95
Anticipated Completion Date:31 August 1998
Government Award: $71,190

Report Period Start Date: September 30, 1995
Report Period End Date: March 31, 1996
Principal Investigators: Hugo S. Caram and Natalie Foster
DOE Project Officer: David J. Wildman MS84-340
U.S. Department of Energy, Pittsburgh Energy Technology Center
Report Issued , November 25,1996

MASTER

1

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SUMMARY OF TECHNICAL PROGRESS:

ABSTRACT: We used glass beads of different sizes as a model system to study the flow enhancing properties of Octadecyltrichlorosilane (OTS). OTS provides $Si(CH_2)_{17}CH_3$ groups that bind with the surface hydroxyl groups to make it hydrophobic. Experimental data showed, indeed, that surface hydrophobicity promotes the flow of wet granular materials. Mixtures of different percentage of silanized/unsilanized particles were prepared for tensile strength measurements. The tensile strength decreased as more silanized particles were added to the samples. The relationship between dimensionless tensile strength and void fraction followed the correlation found by Pierrat (1994). Contact angles were larger for the silanized particles, as compared with unsilanized ones.

INTRODUCTION

Dry granular materials, such as sand and coal, flow easily. However, when they are wet, their ability to flow greatly diminishes as a result of the formation of liquid bridges between the particles (Pierrat, 1994). Millions of dollars are spent annually to minimize the effects of cohesion between the particles and enhance flow in wet granular materials.

Recently, research has focused on improving flow properties of wet granular materials through the development of flow promoters. The use of surfactants, which lower the surface tension of water, have been explored for the enhancement of flow in coal (Pierrat, 1994). Our project probes the use of Octadecyltrichlorosilane (OTS) as a flow enhancer acting at the surface of granular materials by increasing surface hydrophobicity and reducing cohesion between wet particles. Thus we expect a molecular monolayer to dramatically change the bulk properties of the granular mass.

Glass particles with diameters ranging from 1 μm to 2.45mm were used as a model system to study the effects of OTS as a flow enhancer. Contact angle measurements were used to probe the hydrophobicity difference between unsilanized and silanized glass particles. Tensile strength measurements were also used to measure the cohesive force difference as a result of changing surface hydrophobicity. A correlation between dimensionless tensile strength and the void fraction was determined. The results were compared with the correlation found by Pierrat in 1994.
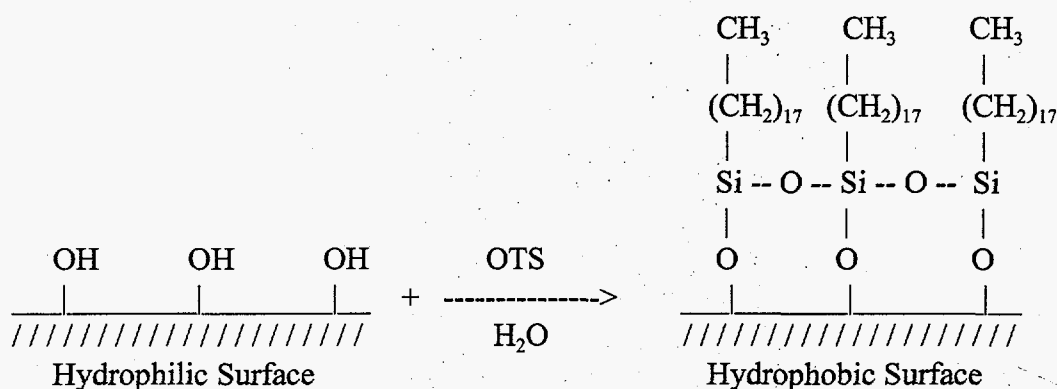
THEORY
The liquid bridge

Water retained by surface effects between two particles forms a liquid bridge. The liquid bridge exerts n attractive force according to its volume and contact angle translates into a cohesive force for the granular media. It is that cohesiveness that make flow difficult. Figure 1a shows an schematic of a liquid bridge on a hydrophilic particle, where a, d and h are the separating distance, the particle diameter and the diameter at the neck of the bridge, respectively and α and θ are the filling and contact angle, respectively. Figure 1b shows the image of an actual liquid bridge obtained using an imaging NMR.

The attractive force is greatly affected by the separating distance and the size of the particles and it weakens as the separating distance and the size of the particles increase. As

3

discussed by Pierrat (1994) the dimensionless attractive force (F/γa) depends only on the dimensionless separating distance (a/d) and the filling and contact angles. The surface tension acts in two ways on the particles. First, as an attractive force along the contact line. Second by creating a " vacuum" or overpressure for concave or convex surfaces. Previous work has dealt with modification of the surface tension. For the same liquid bridge, changing the contact angle, by making the surface hydrophobic, may change the curvature of the bridge possibly creating a repulsive force that will facilitate the flow.

To induce hydrophobicity surfaces containing OH groups such as glass or coal can be treated with Octadecyltrichlorosilane (OTS). The reaction occurs at the surface as follows:

```
                                        CH₃        CH₃        CH₃
                                         |          |          |
                                      (CH₂)₁₇    (CH₂)₁₇    (CH₂)₁₇
                                         |          |          |
                                       Si -- O -- Si -- O -- Si
                                         |          |          |
                                         O          O          O
     OH      OH      OH       OTS        |          |          |
   __|_____|_____|__  + -------->  __|_____|_____|__
   ////////////////////       H₂O      ////////////////////
   Hydrophilic Surface                 Hydrophobic Surface
```

The reaction with OTS causes the surface to be non-wetting by replacing the hydrophilic hydroxyl groups with hydrophobic silane, $(SiCH_2)_{17}CH_3$ groups. As a consequence, the contact angle of a silanized surface is larger than that of an unsilanized surface.

EXPERIMENTAL:
Materials; Methanol, hexane, KOH, iso-propyl alcohol, and parafilm were purchased from Fisher Scientific. Octadecyltrichlorosilane (OTS) was purchased from Aldrich.

Methods:
Glass beads with diameters of 1μm, 88μm, 129μm, 0.54mm, 1.05mm, and 2.45mm were silanized. The base bath for cleaning the glass beads was prepared by mixing 100g KOH, 1.2L iso-propyl alcohol, and about 500 mL water. The glass beads were rinsed several times with tap water until they appeared clean, and soaked in the base bath at room temperature for about 12 hours. The base bath was decanted. The beads were rinsed with an excess amount of tap water, and then three times with deionized water. The cleaned glass beads were then dried over night at room temperature.

The clean glass beads were placed in a large beaker with enough hexane to cover the beads and about 0.5mL of OTS were added. The sample was stirred for 10 minutes to allow uniform surface overage. The excess solution was decanted. The beads were rinsed with deionized water and a few minutes were allowed for polymerization of the OTS. The water was

4

decanted and the beads were cleaned several times with methanol until they appeared free from excess OTS. The beads were air dried overnight.

Granular Material Sample Preparations:

Samples for measuring the tensile strengths were prepared by mixing 0, 25, 50, and 75 percent of silanized beads with unsilanized particles. Samples with pure (100%) silanized particles could not be prepared because they could not be wet or mixed thoroughly. Mixtures of 0.55% and 1.1% of 1µm beads, unsilanized and silanized, with 0.54mm unsilanized beads were also prepared..

Contact Angle Measurements:

The contact angles were measured using a NRL Contact Angle Goniometer (Model 100-00) with a magnification of 23X. The angles were measured at the first contact that the beads had with the water.

Tensile Strength Measurements:

The tensile strengths of the different mixtures were measured using a Parfitt Tensile Tester, running at approximately 0.6mm per minute. The tester uses an oversized split box (81 mm in diameter and 25mm high) to measured the small tensile strengths in these media. It is connected to a data acquisition board PC that reads out the maximum voltage used to break the liquid bridges between the glass particles. Tensile strength measurements were obtained from samples with 0, 25, 50, and 75 percent ratio of silanized/unsilanized beads. Samples with pure (100%) silanized particles could not be prepared because they could not be wet or mixed thoroughly since water would immediately segregate. Mixtures of 0.55% and 1.1% 1mm beads, unsilanized and silanized, with 0.54mm unsilanized beads were also prepared and tested using the same procedure and parameters. The saturation S (fraction of the void fraction ε occupied by water was kept between 23 and 51%. The saturation S was computed from

$$S = (1 - \varepsilon)/\varepsilon \, (\rho_{par}/ \rho_{water})x_w$$

where $x_w = mass_w/mass_{par}$ and ρ_{water} and ρ_{par} are the water and particle densities. Correlations between the dimensionless tensile strength ($\sigma^* = \sigma \, (\delta_p)/\gamma_{water}$) and the void fraction for all tensile tests were obtained, and plotted against Pierrat's correlation. The equation for Pierrat's correlation is:

$$\sigma^* = 7.7977(1-\varepsilon)^{3.0323}$$

RESULTS AND DISCUSSIONS

Liquid Bridges and contact angles:

Figure 2 shows photographs of a hydrophilic (a) and a hydrophobic (b) bridge taken with a 35mm camera attached to a goniometer. These bridges were magnified by 23 times. The beads used for these photos are 2.45mm in diameter. Due to gravity, these photographs are not as symmetrical as the theoretical drawing (Figure 1a). Using these photos, we were able to observe the hydrophobicity imposed by the silane on the surface of the glass beads. The hydrophobicity of the water on the surface indicates the effectiveness of OTS as a possible flow enhancer.

Contact angle measurements were obtained for glass beads with diameters of 0.54mm and 2.45mm, unsilanized and silanized. The contact angle (θ) for the 0.54mm beads was $75°$ without silanization and raised to $102°$ after silanization. Similarly, θ for the 2.45mm beads increased from $79°$ to $111°$ due to silanization.

Tensile Strength Measurements:

We found that the tensile strength (σ) greatly diminished with increasing particle size and surface hydrophobicity. This marked decrease reconfirmed the fact that surface hydrophobicity is capable of lowering the cohesion between the surface and the water. When the beads were silanized with OTS, all of the free OH groups were indeed covered by the silane ($Si(CH_2)_{17}CH_3$).

Since the tensile strength of silanized particles was too low to be measured in with the available tools, the effect of adding treated (silanized) particles to untreated material was studied. The ratio between the tensile strength of the sample to the tensile strength of the untreated granular material as a function of the volume fraction of silanized particles is shown in figure 3. For both particle sizes ($d_p = 129\mu m$ and 0.54mm), the results were very consistent. As the percentage of silanized particles increased, the values for σ dropped almost linearly with the fraction of silanized beads. Details are given in tables 1 and 2. The samples with 10% water by weight had a percent saturation ranging from 36.5 to 51.1 for the 129 μm beads, and 46.7 to 61.1 for the 0.54mm beads, and void fraction, ε, ranging from .36 to .44 and .32 to .37 for the 129μm beads and 0.54mm beads, respectively. The 23.9% saturation samples included samples with a saturation of 23.9% and ε of 0.46 for both sizes.

When plotted against Pierrat's correlation (Figure 4), the dimensionless tensile strength obtained from the 129μm beads followed this curve closely. The 0.54mm beads, however, were farther off, because the values for the dimensionless tensile strength were on a much higher range, although σ was lower for the larger beads.

It was conjectured that the addition of fine silanized beads to the granular media would create a hydrophobic cover for the large beads. A small amount of silanized 1μm beads were mixed with 0.54mm unsilanized beads, σ was predicted to be lower than that of a sample with 100% unsilanized 0.54mm beads, because we assumed that the surfaces of the 0.54mm beads would be covered by the silanized 1μm particles. The results, shown in figure 5 and table 3, show no significant trend. At 0.55% of 1μm beads (half covered), σ was 842 Pa, whereas the

6

fully covered beads (1.1% of 1μm beads) resulted in a smaller σ of 813 Pa. Another set of tests were run, but with unsilanized 1μm beads and unsilanized 0.54mm beads. The results were contrary to our prediction. The tensile strength also dropped as the percentage of 1μm beads increased, but more significantly, from 681 Pa to 456 Pa when the amount of 1mm beads were increased from 0.55% to 1.1% (Figure5). Since 1μm beads were unsilanized this time, we expected an increase when we increased the amount of the small beads, because it should require more force to break the cohesion between smaller particles. This result indicated that the 1μm particles did not behave as we had predicted. It is possible that the silanized 1μm particles did not stay on the surfaces of the unsilanized 0.54mm beads because of the water on these hydrophilic surfaces. This reasoning, however, does not explain why the tensile strength for the mixture with both particles unsilanized also decreased as the percentage of 1μm particles increased.

CONCLUSIONS

Glass beads were indeed a valid model to use for our studies on the cohesive properties of coal. Previous experimental work showed that coal and glass particles could be silanized the same way. Silanized coal and glass particles exerted similar properties. We concluded that silanization is an effective method of increasing surface hydrophobicity. the contact angle increased and tensile strength decreased with increasing hydrophobicity. Increasing surface hydrophobicity was an effective way to diminish the cohesion problem. Mixing large unsilanized particles with silanized smaller particles did not have a major effect on solving our problems.

REFERENCES
1. Angst, David L., "Moisture Absorption Characteristics of Organosiloxane Self-Assembled Monolayers," in Langmuir, vol 7(10):2236-2242, Mar 1991.
2. Gould, Robert F.(ed), CONTACT ANGLE Wettability and Adhesion, American Chemical Society, Washington, 1964.
3. Hartland, Stanley & Hartley, Richard W., Axisymmetric Fluid-Liquid Interfaces, Elsevier Scientific Publishing Company, Amsterdam, 1976.
4. Pierrat, Patrice, The Flow Properties of Wet Granular Materials, Ph.D. Thesis at Lehigh University, 1994.

TABLE 1: TENSILE TEST RESULTS FOR 129μm BEADS

$\rho = 2.58 \text{g/cm}^3$

%sil/un	height(	hxD	ε	% Sat	Force	σ (Pa)	σ*	σ/σ$_{max}$
0	.01213	.000982	.44	36.5	1.348	1373	2.46	1
25	.01164	.000943	.42	39.8	0.724	768	1.38	0.56
50	.01106	.000896	.36	50.9	0.448	500	0.90	0.36
75	.01055	.000855	.36	51.1	0.138	162	0.29	0.12
0	.01404	.001137	.46	23.9	0.981	862	1.55	1
25	.01229	.000995	.46	23.9	0.376	378	0.68	0.44
50	.01198	.000970	.46	23.9	0.324	334	0.60	0.39
75	.01178	.000954	.46	23.9	0.162	170	0.30	0.20

TABLE 2: TENSILE TEST RESULTS FOR 0.54mm BEADS

$\rho = 2.46 \text{g/cm}^3$

%sil/un	height(	hxD	ε	% Sat	Force	σ (Pa)	σ*	σ/σ$_{max}$
0	.01124	.000911	.37	46.7	.757	831	6.23	1
25	.01028	.000833	.31	61.1	.472	567	4.25	.68
50	.01056	.000855	.33	56.3	.395	462	3.46	.56
75	.01043	.000844	.32	58.4	.243	288	2.16	.35
0	.01455	.001179	.46	23.9	.733	622	4.66	1
25	.01713	.001388	.46	23.9	.624	450	3.37	.72
50	.01460	.001183	.46	23.9	.476	403	3.02	.65
75	.01460		.46	23.9	.424	359	2.69	.58

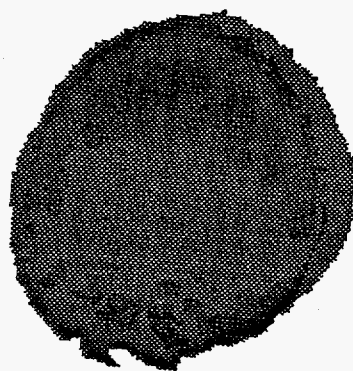## TABLE 3: TENSILE TEST RESULTS FOR MIXED BEADS
(0.54mm unsil and 1μm unsil/sil)

$\rho = 2.46 \text{g/cm}^3$

% 1mm	height	hxD (m^2)	ε	% Sat	Force (N)	σ	σ*
.55 (unsil)	.0145	.001175	.46	23.9	.80	681	5.11
1.1 (unsil)	.0143	.00116	.46	23.9	.53	456	3.42
.55 (sil)	.0144	.001166	.46	23.9	.981	842	6.31
1.1 (sil)	.0144	.001166	.46	23.9	.948	813	6.10
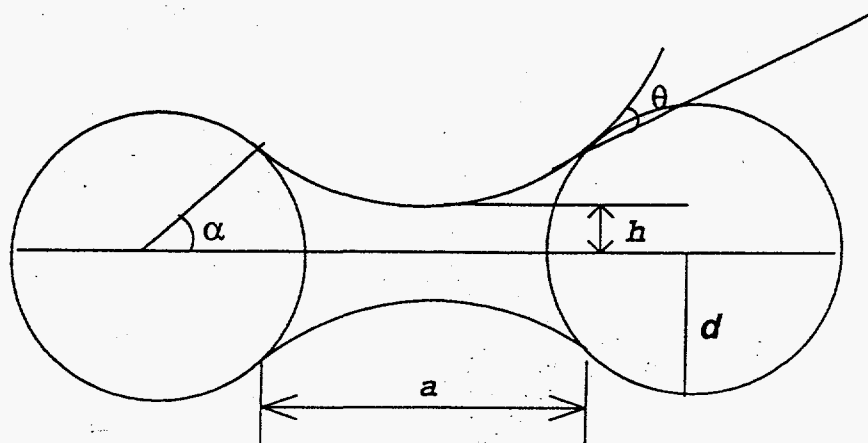
Figure 1a: Theoretical Hydrophilic Liquid Bridge

Dimensions: 8 slices, 128x128, 0.4mm thickness

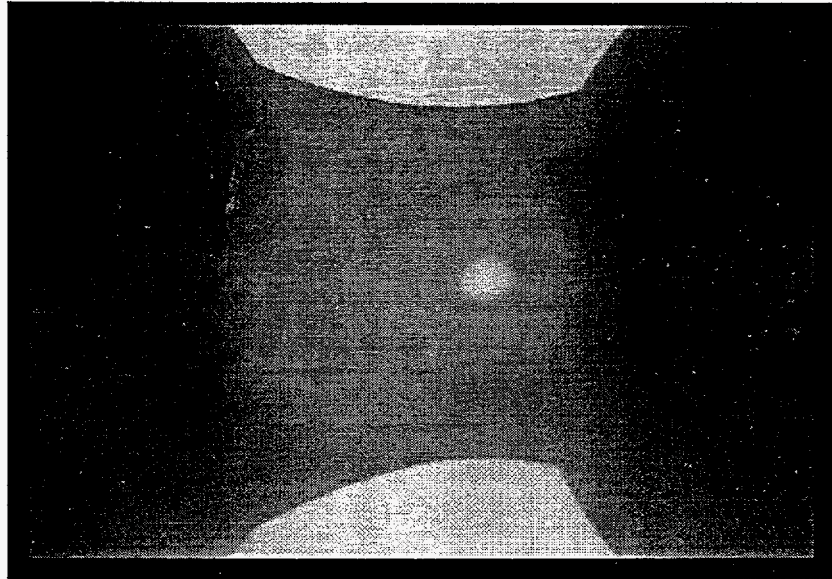**Figure 1b: Hydrophilic Liquid Bridge Taken as a NMR Image**

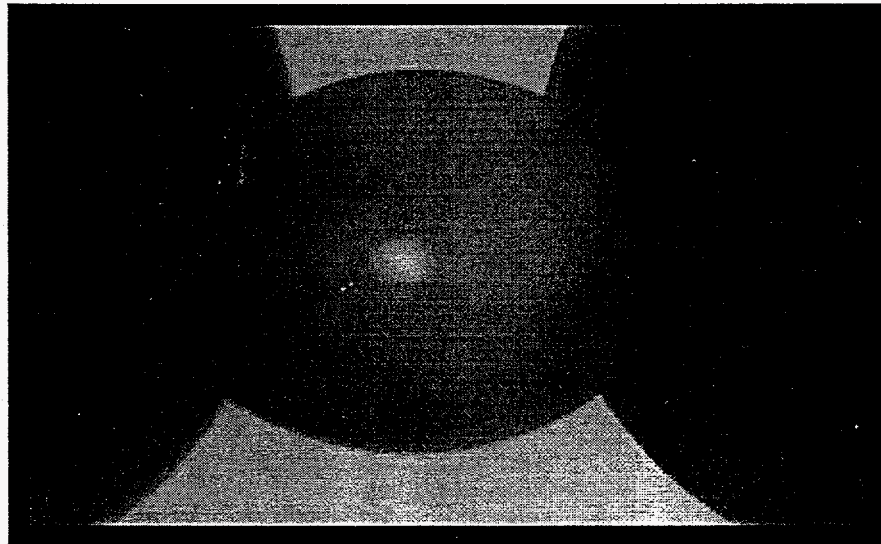Figure 2a: Hydrophilic Liquid Bridge Between
Two 2.45mm Glass Particles

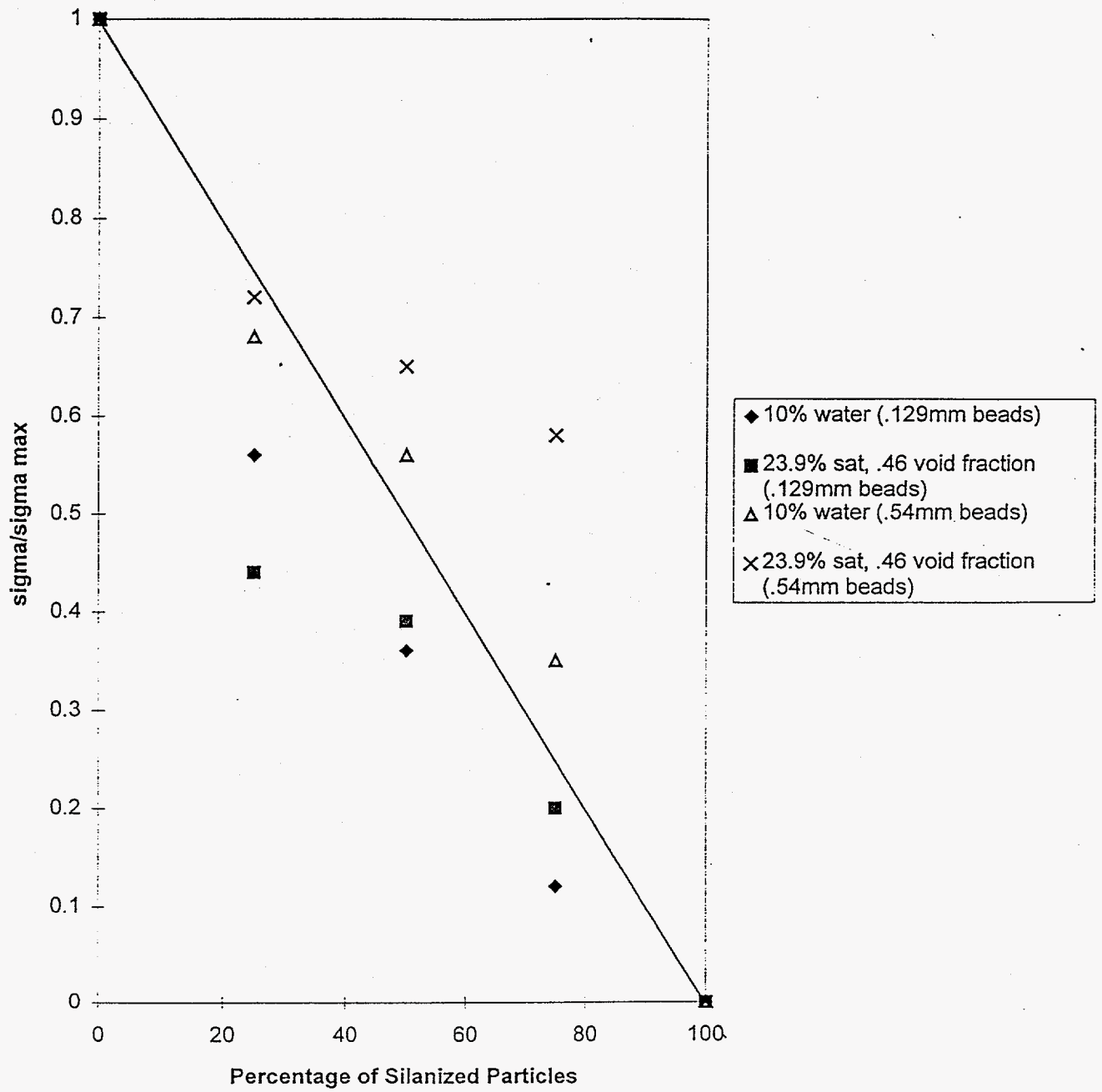Figure 2b: Hydrophobic Liquid Bridge Between
Two 2.45mm Glass Particles

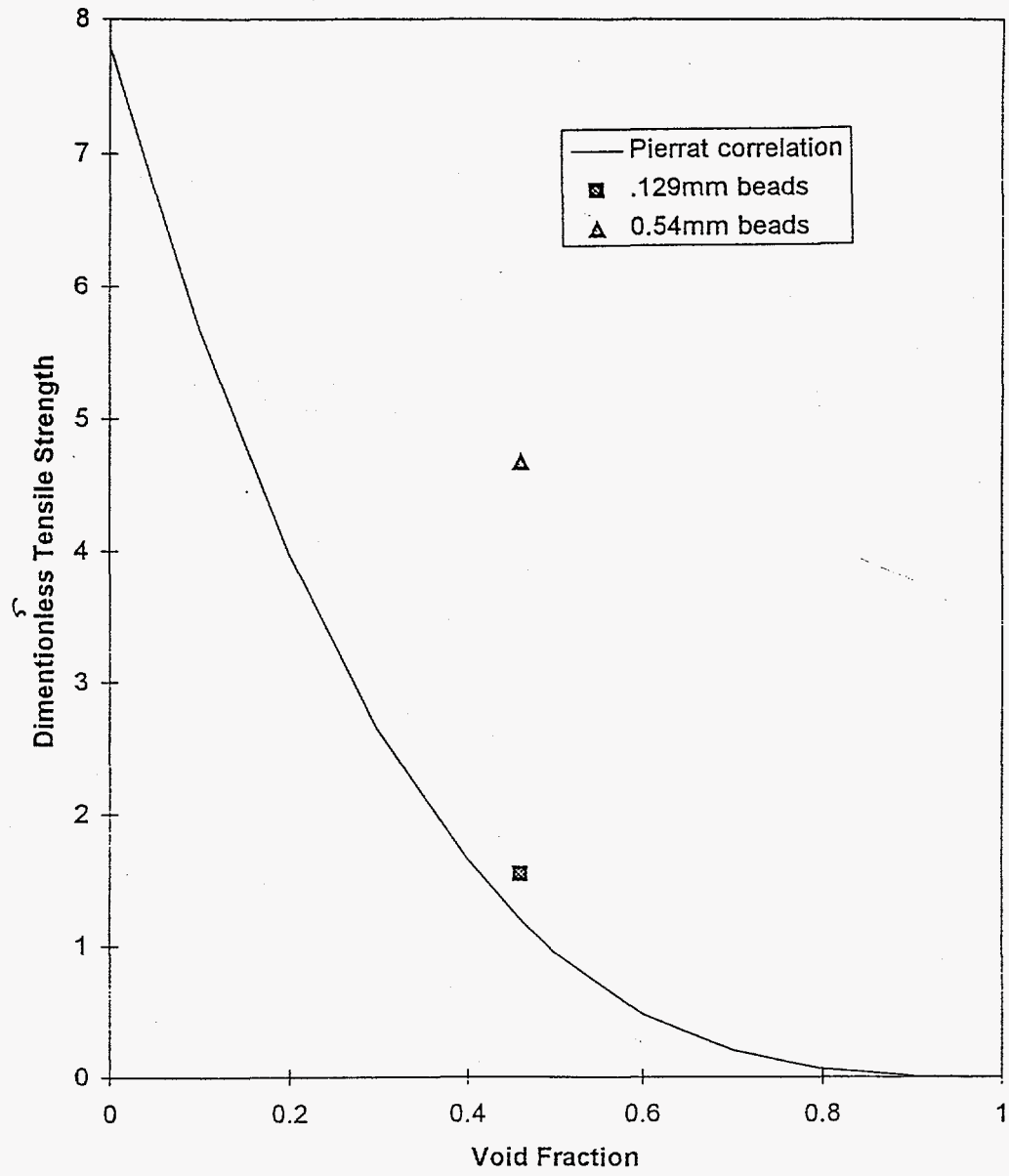Figure 3:Correlation between tensile strength and percentage of silanized particles.

Figure 4:The tensile strentgth of 129μm and 540μm particles against the Pierrat correlation.