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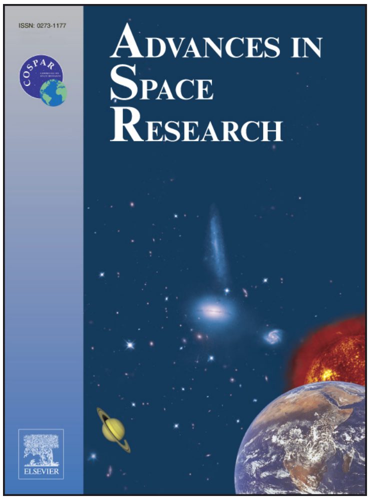

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Geopolymers from lunar and Martian soil simulants

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Abstract

This work discusses the geopolymerization of lunar dust simulant JSC LUNAR-1A and Martian dust simulant JSC MARS-1A. The geopolymerization of JSC LUNAR-1A occurs easily and produces a hard, rock-like, material. The geopolymerization of JSC MARS-1A requires milling to reduce the particle size. Tests were carried out to measure, for both JSC LUNAR-1A and JSC MARS-1A geopolymers, the maximum compressive and flexural strengths. In the case of the lunar simulant, these are higher than those of conventional cements. In the case of the Martian simulant, they are close to those of common building bricks.

Keywords: JSC LUNAR-1A; JSC MARS-1A; Mars; Moon; geopolymer.

1. Introduction

Plans for long-term planetary or lunar outposts require the creative use of the available resources for sustainable human existence outside our planet. In this context, building materials deserve special attention since they are intrinsically heavy and usually required in large quantities. Therefore, their on-site production would reduce the amount of payload sent from Earth considerably.

As a building material for lunar structures, researchers have proposed Lunarcrete (Happel 1993); a concrete where lunar regolith, instead of sand, is used as an aggregate. An even more radical solution –because both the aggregate and the binder come from the regolith– would be the on-site production of building material by geopolymerization. With some notable exceptions (e.g. Montes et al. 2015), however, little attention has been given to the geopolymerization of the lunar regolith, and no attention at all has been given to the geopolymerization of the Martian regolith. NASA has a renewed commitment to human missions to Mars, including investments in planetary research, enabling life support technologies, as well as the development of spacecraft and launch systems capable of carrying humans to Mars. Living and working on Mars is considered a solvable challenge, and the ability to construct human-habitable structures using planetary resources is a significant aspect of the problem.

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This study focuses on the geopolymerization of both lunar (JSC LUNAR-1A) and Martian (JSC MARS-1A) dust simulants. In fact, the geopolymerization of JSC LUNAR-1A has generated new scientific questions. Can JSC MARS-1A geopolymerize as well? How high are the compressive and tensile strengths of the Martian geopolymer compared to that of the lunar geopolymer? How do they compare to commercially available cement?

2. Geopolymerization

Geopolymers are a class of cementitious materials formed by the reaction of an alkaline solution with an aluminosilicate source such as fly ash or red mud, which today are considered as a potential alternative for replacing traditional structural materials (Davidovits 1994).

The process of geopolymerization starts with silalate (–Si–O–Al–) or silalate-siloxi (–Si–O–Al–O–Si–) monomers in solution that join together to form inorganic polymers with properties similar to those of Portland cement. In general, geopolymerization is a complex process, involving three main steps: (i) alkali activation, which consist in the dissolution of amorphous aluminosilicates by alkali to produce monomers; (ii) reorientation, which consists in the transportation, orientation, and condensation of monomers into oligomers; and (iii) polycondensation, where the whole system hardens into an inorganic polymeric structure (Xu and Van Deventer 2002).

Any material with high fractions of silica and alumina in amorphous (glassy) form could, in principle, geopolymerize. The composition of both JSC LUNAR-1A and JSC MARS-1A is shown in Table 1 (Allen et al. 1998, Gustafson 2009); in both cases, the major components are SiO_2 and Al_2O_3. Moreover, both simulants are collected form glassy volcanic ashes and have a high amorphous content. Ideally, geopolymers should have a stoichiometric Si/Al ratio of 1, 2 or 3 (Davidovits 1994): the lunar simulant has a Si/Al ratio around 2.5, the Martian around 1.6. All these considerations suggest that, at least in theory, both Lunar and Martian simulants should react with alkaline solutions to form geopolymers.

We prepared six samples (three with JSC LUNAR-1A and three with JSC MARS-1A) following the method given by Xu and Van Deventer 2002:
Sample 1, 30 g of simulant, 7 mL solution of water 8 M NaOH.
Sample 2, 20 g of simulant, 10 g of K_2SiO_3, 7 mL solution of water 8 M NaOH.
Sample 3, 50 g of simulant, 10 g of K_2SiO_3, 20 mL solution of water 4 M NaOH.
In Sample 2 and 3, K-silicate (K_2SiO_3) was added to obtain samples with various Si/Al ratios. NaOH solutions with different concentrations were used to obtain samples at various pH. After blending the different materials, a viscous fluid was obtained. The final mixture was dried at constant temperature of 80°C for 3 hours in a silicone stamp (8x20x40 mm) and cured at room temperature for another 28 days.

The resulting product, for all three samples containing JSC LUNAR-1A, was a rock-like solid as expected in the case of geopolymerization. On the contrary, none of the samples containing JSC MARS-1A agglomerated, but produced a loosely cohesive assembly that easily crumbled when dry.

2.1 Effect of Milling

Does this negative result imply altogether that geopolymers from Martian simulant cannot be produced? JSC MARS-1A has a good content of alluminosilicates, the Si/Al ratio is acceptable, and volcanic ashes with composition similar to JSC MARS-1A are known to geopolymerize producing materials with high mechanical strength (Tchakoute et al. 2013).

The lack of geopolymerization could originate from the larger size of JSC MARS-1A particles. The mean (volume averaged) particle size of the lunar simulant is around 190 µm, while that of the Martian is 295 µm. This indicates a lower contact area between the NaOH solution and the JSC MARS-1A particles and, therefore, slower alkali activation.

In order to test this hypothesis, the dust was milled to reduce the particle size and, at the same time, enhance reactivity by mechanical activation (Terzić et al. 2014). A planetary mill Pulverisette 5 by Fritsch GmbH was used for 30 minutes at 200 rpm followed by a 125µm sieve to remove any larger particles left. This procedure was adopted for both simulants, and the new size distributions measured with a Malvern Mastersizer Particle Size Analyzer. Milling produced a tenfold reduction of the mean particle size, which decreased to 19 µm in the case of JSC LUNAR-1A and to 28 µm in the case of JSC MARS-1A. After milling, the particles of the two simulants present a very different morphology as indicated by Figure 1 (images obtained with a SEM microscope Hitachi TM3030). The lunar particles have very sharp and jagged edges, the Martian particles tend to be more round.

The same procedure used before was applied to the milled simulants and, this time, both JSC LUNAR-1A and JSC MARS-1A samples produced solid blocks (Figure 2).

2.2 FTIR data

To verify that the hardening of the material is actually due to geopolymerization, FTIR spectra of the original JSC LUNAR-1A and JSC MARS-1A dusts were compared with the corresponding agglomerated samples. Absorbance profiles were obtained with a Bruker Tensor 27 FTIR Spectrometer.

The peaks highlighted in Figure 3 are typical of geopolymers (Montes et al 2015, Zhang et al. 2012, Arioz et al. 2013, Cătănescu et al 2012, Lee et al 2003). The strong peak at ~1000 cm^{-1}

(labelled **A** in Figure 2) includes T-O-Si (T = Al or Si) asymmetric stretching vibrations within the TO_4 tetrahedra typical of the amorphous aluminosilicates and is considered to be the fingerprint of geopolymerization (Montes et al 2015, Arioz et al. 2013, Lee et al 2003). Atmospheric carbonation is evident at around 1430 cm^{-1} (peak **C**) (Montes et al 2015, Arioz et al. 2013, Cătănescu et al 2012). Peak **B** refers to the symmetric Si-O bonds and its increase can be associated with the addition of soluble silicates during the preparation of the samples (Lee et al 2003). The shifting of the main band **A** to smaller wave numbers suggests the silica solubilisation and polycondensation processes and is also typical of geopolymerization (Montes et al 2015, Zhang et al. 2012, Arioz et al. 2013, Cătănescu et al 2012, Lee et al 2003). Moreover, the disappearance of the bands at around 600 cm^{-1} (band **F**) points out the consumption of silicates or aluminosilicates glasses (Cătănescu et al 2012, Lee et al 2003). The bands indicated with **E** are attributed to the stretching vibrations of –OH, while point **D** refers to the bending vibrations of H-O-H (Montes et al 2015, Arioz et al. 2013, Cătănescu et al 2012).

3. Strength of the JSC LUNAR-1A and JSC MARS-1A geopolymers

Once geopolymers are produced from both lunar and Martian simulants, we want to evaluate their strength in comparison with traditional building materials such as cement. There are several types of material strengths that can be tested: Montes et al. 2015, for instance, measured the compressive strength of the lunar geopolymers. This is the typical test performed on building materials such as concrete with a much higher compressive strength than tensile strength.

In this study, we assess both compressive and tensile strength for both JSC LUNAR-1A and JSC MARS-1A geopolymers. In the case of tensile strength, we actually tested the flexural strength, which is often used as a measure of tensile strength (Young and Budynas 2001).

Standard tests for both compressive and flexural strength are based on relatively large samples and usually require quantities of material larger than those available to us. For this reason, we based our analysis on tests that need less quantities of material. We also performed these tests on conventional cement (Tarmac high performance Cement) and compared the results between cement, lunar polymer, and Martian polymer.

3.1 Compressive strength

Standard test for compressive strength of concrete specimens are based on cylindrical samples with diameters between 10 and 15 cm and heights between 20 and 30 cm, or on standard size 10 cm concrete cubes. In order to use a lesser quantity of simulant, the compressive strength of cubes of approximately 1 cm of length was measured. We prepared the samples with the milled simulant (for both JSC LUNAR-1A and JSC MARS-1A) and solutions at different NaOH concentrations (see Table 2); K_2SiO_3 was not added to any of the samples.

The cubes were tested to failure in compression by an Advanced Materials Testing Machine LS 100 kN Plus by Lloyd Instruments Ltd. In Table 2, the maximum compressive strength is calculated by averaging the results obtained with a varying number of tests (also indicated in Table 2). The maximum compressive strength is achieved in the case of Luna-8M (18.4±1.6 MPa based on 7 tests/samples) and it is even higher to that of cement. In general, the compressive strength is larger for the samples produced using 8M NaOH solutions for both the lunar and the Martian simulants, but JSC MARS-1A, overall, results in a weaker geopolymer.

3.2 Flexural strength

The transverse bending test is most frequently employed test for measuring the flexural strength of concrete samples. Also in this case, we prefer a technique that requires less material. The milled powder was mixed with a 8 M sodium hydroxide solution, which produced the geopolymers with higher compressive strength. Ten geopolymer disks (diameter 12 mm, thickness ~ 1mm) for each simulant were made. Table 3 displays the composition of the lunar and Martian geopolymers, along with a conventional cement sample (Tarmac high performance Cement, as before) used for comparison purposes.

A Stable Micro Systems TA.XTplus texture analyser was used to test the samples; the disks are placed at the centre of a metal plate with a circular hole of 9 mm and the probe measures the force required to break each sample as illustrated in Figure 4. From the break-up force, the maximum flexural strength was estimated from the formula (Young and Budynas 2001)

$$\sigma_{\max} = \frac{F}{h^2}\left[0.6201\ln\left(\frac{d}{d_0}\right) + 0.477\right] \tag{1}$$

Where F is the maximum force required to break the sample, h is the thickness of the sample, d the diameter of the hole and d_0 the diameter of the probe

For each material, the tests were repeated with ten different specimens; the averaged maximum force required to break each type of disk is reported in Table 3 together with the respective standard deviation.

The lunar geopolymer is by far the strongest material of the three, while the Martian geopolymer is almost of similar strength to traditional cement. It is also worth noting that upon breakage, the lunar geopolymer broke cleanly into a few fractured pieces whereas the

Martian and cement samples crumbled into pieces of much larger size distribution down to the powder-like scale.

4. Discussion

While the lunar dust simulant geopolymerizes as it is, the Martian simulant requires milling. Milling reduces the particle size and has a twofold effect on the geopolymerization process: it increases the contact area with the alkaline solution, and increases the alluminosilicates reactivity. The former occurs because smaller particles have a larger surface area per unit volume than larger particles. The latter occurs because, during milling, fractures and break-up arise preferentially at the defects of the crystal structure (Chunlong et al. 2010). Defects are the chemically most active parts of the structure that, in this way, are exposed to the particle surface.

High chemical reactivity means high degree of geopolymerization and, in turn, high compressive strength. Actually, compressive strength is often used as a measure of success of geopolymerization (Xu and van Deventer 2003). Therefore, the higher compressive strength of the lunar geopolymers can be explained by the higher reactivity of JSC LUNAR-1A with respect to JSC MARS-1A.

However, there are other two factors to consider. Firstly, experiments indicate that the compressive strength of geopolymers increases with the Si/Al ratio (Duxon et al. 2007); the Si/Al ratio of JSC LUNAR-1A is actually higher than that of JSC MARS-1A. Secondly, due to the higher particle size, the Martian geopolymer is less dense and more porous than the lunar geopolymer. The densities of the JSC LUNAR-1A and the JSC MARS-1A geopolymers are respectively 2.6 g cm^{-3} and 1.8 g cm^{-3}. Therefore, there is less material in the Martian samples and actually the higher porosity of the Martian geopolymers, after breakage, can be appreciated with the naked eye.

5. Conclusions

The lunar geopolymer outperforms cement in both compressive and flexural strength tests. Moreover, both lunar and Martian geopolymers do not show a drastic reduction of flexural strength with respect of compressive strength, as is the case with cement.

The Martian geopolymer is clearly the weakest material when it comes to compressive strength. This has been associated to a low reactivity of JSC MARS-1A. The reactivity of a given oxide depends on the binding energies of its crystal (or amorphous) structure. JSC MARS-1A was designed to match the available information on the Martian soil composition. However, details about its reactivity are unknown and, therefore, we do not possess enough information to establish if the chemical activity of JSC MARS-1A is representative of the real regolith.

From a certain point of view, we consider the conditions of Martian geopolymerization tested in this study a sort of unfavourable scenario. In the samples tested for compressive and flexural strength, we limited milling to 30 minutes; we did not perform any preliminary thermal activation; and we did not add K_2SiO_3 or any other additive. We chose this course of action to test geopolymerization under conditions maximizing in-situ resource utilization.

Under these circumstances, the compressive strength of the Martian geopolymer is not comparable to concrete. Nonetheless, it is comparable to other building materials such as common clay bricks, whose compressive strength is 3.5 MPa. This means that, even in this unfavourable scenario, geopolymers made from Martian regolith could be used as building material and could play a role in the future colonization of the red planet.

6. References

Montes C., Broussard K., Gongre M., Simicevic N, Mejia J., Tham J., Allouche E., Davis G. (2015) Evaluation of lunar regolith geopolymer binder as a radioactive shielding material for space exploration applications, *Adv. Space Res.* **56**:1212–1221

Davidovits J. (1994), Geopolymers: Man-Made Rock Geosynthesis and the Resulting Development of Very Early High Strength Cement, *J. Materials Education* **16**:91–139

Xu H., van Deventer J. (2002) Geopolymerisation of multiple minerals *Minerals Engineering* **15**:1131–1139

Allen C.C., Jager K.M., Morris R.V., Lindstrom D.J., Lindstrom M.M., Lockwood J.P. (1998) Martian soil simulant available for scientific educational study *EOS* **79**. 405-409

Gustafson, R. (2009) JSC-1A lunar regolith simulant availability and characterization *Proc. 2009 Lunar Regolith Simulant Workshop*, NASA Marshall Space Flight Center, Huntsville, AL

Happel J. (1993), Indigenous materials for lunar construction, *App. Mec. Rev.* **46**:313–325.

Tchakoute H., Elimbi A., Kenne D., Mbey J. A., Njopwouo D. (2013) Synthesis of geopolymers from volcanic ash via the alkaline fusion method: Effect of Al_2O 3/Na_2O molar ratio of soda-volcanic ash, *Ceram. Int.* **39:** 269–276.

Terzić A., Andrić L., Mitić V. (2014) Assessment of intensive grinding effects on alumina as refractory compound: Acceleration of γ to α phase transformation mechanism, *Ceram. Int.* **40**:14851–14863

Zhang Z., Wang H., Provis J. L. (2012) Quantitative study of the reactivity of fly ash in geopolymerization by FTIR *J. Sustainable Cem. Based Mater.* Cement-Based Materials **1**:154–166

Arioz E., Arioz Ö., Koçkar Ö. M. (2013) The Effect of Curing Conditions on the Properties of Geopolymer Samples *Int. J. Chem. Eng. Appl.* **4**:423–426

Cătănescu I., Georgescu M., Melinescu A. (2012) Synthesis and characterization of geopolymer binders from fly ash *U.P.B. Sci. Bull. B* **74**:1–14.

Lee W., van Deventer J. (2003) Use of Infrared Spectroscopy to Study Geopolymerization of Heterogeneous Amorphous Aluminosilicates *Langmuir* **19**:8726–8734.

Young W., Budynas R. (2001) Roark's Formulas for Stress and Strain Hardcover (7th edition) McGraw-Hill.

Xu H., van Deventer J. (2003). Effect of Source Materials on Geopolymerization *Ind. Eng. Chem. Res.* **42**:1698-1706.

Chunlong K., Toshinori T. (2010). Zeolite nanocrystas prepared from zeolite microparticles by a centrifugation – assisted grinding method *Chem. Eng. Process.* **49**:809–814.

Duxson P., Mallicoat S.W., Lukey G.C., Kriven W.M., van Deventer J. (2007) The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers *Colloids Surf. A* **292**:8–20

TABLES

Oxide	JSC LUNAR-1A [wt%]	JSC Mars-1A [wt%]
SiO_2	46.7	43.7
Al_2O_3	15.8	23.4
CaO	9.9	6.2
MgO	9.4	3.4
FeO	8.17	3.5
Fe_2O_3	12.5	11.8
Na_2O	2.8	2.4
TiO_2	1.7	3.8
K_2O	0.8	0.6
P_2O_5	0.7	0.9
MnO	0.19	0.3

Table 1: Chemical composition of JSC LUNAR-1A and JSC MARS-1A.

Sample name	Quantity of simulant [g]	NaOH conc. [M]	Num. of tests/samples	Average side [mm]	Compressive strength [MPa]
Cement	38	0	10	9.0	12.6±1.6
Luna-2M	24	2	8	8.8	2.0±0.6
Luna-4M	24	4	7	9.4	3.7±0.7
Luna-6M	24	6	7	9.8	7.8±0.5
Luna-8M	24	8	7	9.3	18.4±1.6
Mars-2M	20	2	5	9.4	1.4±0.3
Mars-4M	20	4	6	9.2	1.0±0.3
Mars-6M	20	6	7	9.0	0.7±0.2
Mars-8M	20	8	8	9.1	2.5±0.3

Table 2. Geopolymer cubes composition and maximum compressive strength

Solid	Liquid	Composition [g/ml]	Maximum force [N]	Flexural strength [MPa]
JSC LUNAR-1A	8 M NaOH	4.3	17.9 ± 2.7	13.0 ± 3.7
JSC MARS-1A	8 M NaOH	2.5	5.0 ± 1.8	3.6 ± 1.3
Standard cement	Deionised water	4.0	6.7 ± 1.2	4.8 ± 0.9

Table 3. Geopolymer composition and force required to break the solid geopolymer and cement disks. The final values of flexural strength are calculated on the basis of 10 tests/samples.

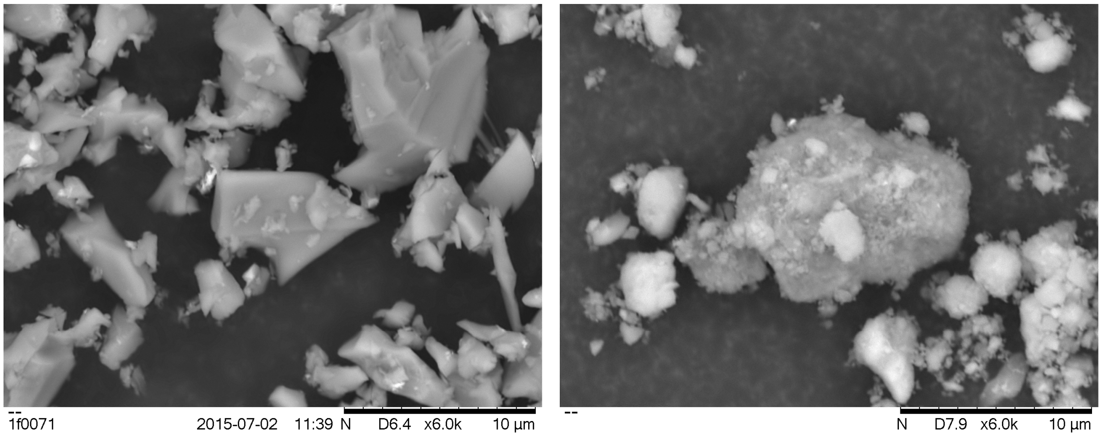
FIGURE CAPTIONS

Figure 1. SEM images of the milled JSC LUNAR-1A (a) and JSC MARS-1A (b).

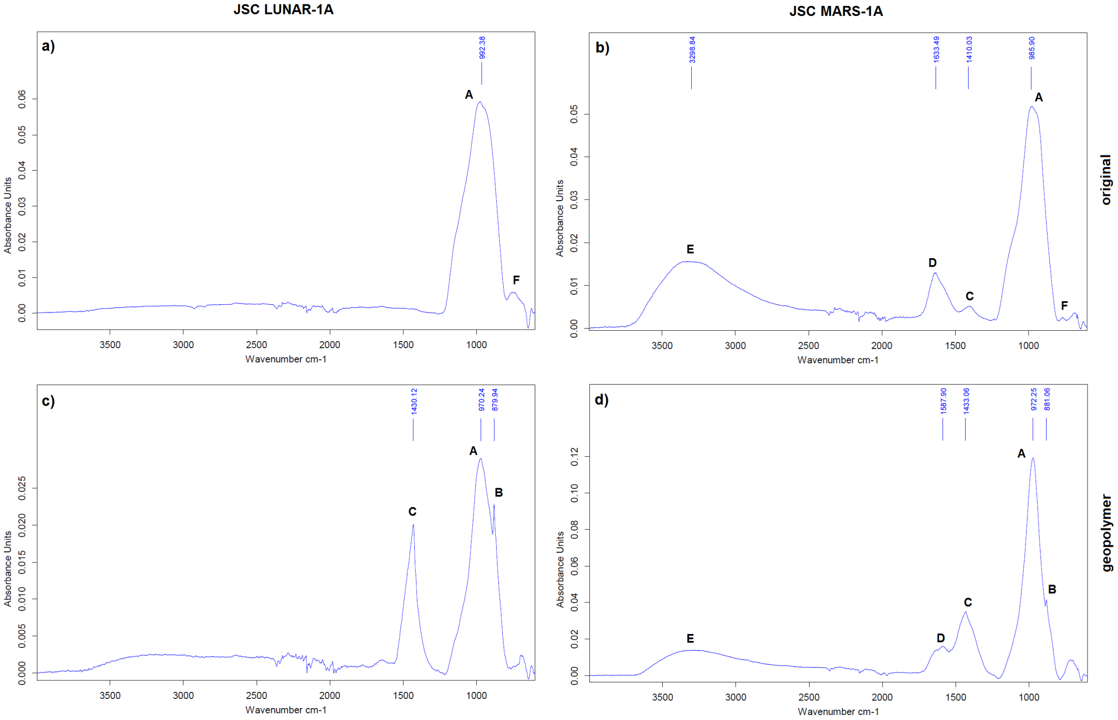
Figure 2. Blocks of JSC LUNAR-1A (left) and JSC MARS-1A (right) geopolymers

Figure 3. FTIR data of lunar and Martian simulants before and after geopolymerization (Sample 2).

Figure 4. Test used to estimate the flexural strength



(a) (b)


JSC LUNAR-1A
JSC MARS-1A
original
geopolymer
a)
992.38
A
F
b)
3298.84
1633.49
1410.03
985.90
E
D
C
A
F
c)
1430.12
970.24
879.94
C
A
B
d)
1587.90
1433.06
972.25
881.06
E
D
C
A
B
Absorbance Units
Wavenumber cm-1
3500
3000
2500
2000
1500
1000
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.000
0.005
0.010
0.015
0.020
0.025
0.08
0.10
0.12

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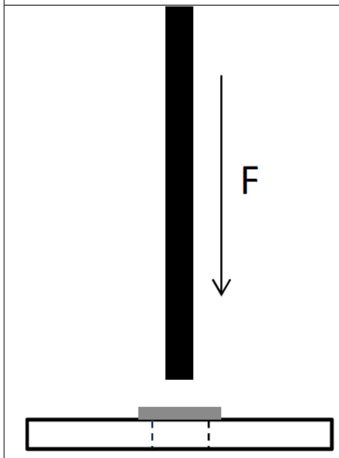
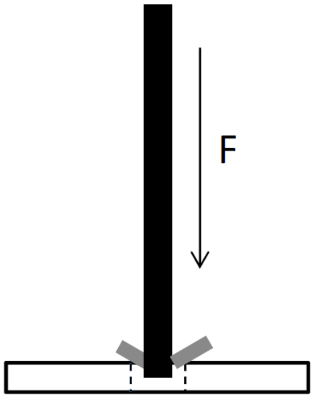
<tr><td rowspan="11">
</td><td rowspan="11">
</td><td>12 mm</td></tr>
<tr><td>Cylinder stainless probe diameter :</td></tr>
<tr><td>6 mm</td></tr>
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<tr><td>9 mm</td></tr>
<tr><td>Load Capacity cell:</td></tr>
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