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Measurement of the saturated surface dry state of fines

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Abstract: New materials for use in concrete or in the construction sector are constantly appearing. These materials may have different composition or properties from the existing materials. This challenges the test methods since they may not be appropriate for the new materials. In this paper a test method for measuring the saturated, surface-dry (SSD) water absorption of particles in the size range 1-100 µm is described. Quantitative identification of the SSD state is very important for the water balance of concrete materials, however, existing test methods such as EN and ASTM does not work for particles in this size.

INTRODUCTION

The water balance is a fundamental issue throughout the life of concrete: During mixing water has a major influence on the ability of the concrete ingredients to mix homogenously, during placement water is the single most important parameter, which controls the workability of the fresh concrete, during hardening access of free water to enable cement hydration is vital, and for the hardened concrete water and its state of binding have a strong influence on many basic concrete properties: dimension, density, strength, durability etc. Raw materials used for concrete need to be carefully evaluated for their ability to retain or give off water, since this has to be taken into consideration in the concrete mix design.

In the recent years a strongly increasing number of different powderous materials such as pozzolans and mineral fillers have been introduced as concrete raw materials either for environmental or economic reasons or because of the positive properties they may contribute with. However, these materials are of very different nature and there may be a lack of test methods to evaluate their properties. This paper suggests a method for identifying the saturated-surface-dry state of filler. The technique has been tested on a material with particle sizes in the range 1-100 µm where the standard methods for fine aggregate such as EN and ASTM are not operational.

BACKGROUND AND CONCEPT

Concrete is very sensitive to changes in its water content, and also the internal exchange of water between aggregate and the cement paste plays a major role. On one hand if dry aggregate is used for concrete mixing, water will be absorbed into the open aggregate porosities from the cement paste leading to a reduced w/c ratio. On the other hand if the aggregate contains water beyond its saturated-surface-dry state (SSD) it will release water to the cement paste and increase the w/c-ratio. This will affect the properties of both the fresh and the hardened concrete. Aggregate particles usually contain some porosity – normally a few percent – but in extreme cases it may be 90% of the aggregate particle volume, even as open pores [1]. Since the aggregate by volume typically occupies 70% of the concrete, a large amount of water can potentially be accommodated in the aggregate pores, and for concrete mix design the water balance in relation to the aggregate is a central parameter to take into consideration.

For modern concrete – decreased w/c ratio and addition of supplementary cementitious materials – the water balance is particularly important, due to its lower water content and in general finer pore structure. Such concrete have undergone optimization towards higher strength, improved workability, better durability etc., and this development has put up stronger requirements for the manufacturing process of concrete: mix design, curing and not the least the concrete ingredient properties. This, however, has a built-in schism as in parallel concrete technology is forced to use new and increasingly more ill-defined materials due to shortage of resources or for environmental reasons. In relation to this it is important that technical standards – specifications, test methods, practices and definitions – cover the de facto needs of modern concrete technology.

Particle sizes

ASTM C125 [2] defines sand ("Fine aggregate") as the portion of particles in the size range 74 µm - 4.75 mm, and stone ("Coarse aggregate") as the portion of particle above this size range. In other standards similar definitions are used, though the size ranges may be different such as e.g. 63 µm - 4 mm for the fine aggregate according to EN 1097 and EN 12620 [3,4]. Within concrete technology the

designation for particle sizes below the lower size limit for sand is not well-established, but within geotechnics the 2 µm - 60 µm fraction is termed "silt" and below 2 µm "clay", though in addition to size restrictions these terms are normally linked to a certain mineral origin. These terms are not used in concrete technology as reference for particle sizes. The Danish concrete application standard DS 2426 [5] defines particles of sizes below 250 µm as "filler", i.e. a part of the sand fraction will be a filler. In this paper the term used for particles finer than sand is "filler". Filler thus includes e.g. Portland cement.

Definition of the saturated-surface-dry state of aggregate
"Saturated-surface-dry" or SSD refers to a moisture condition where the open pores of a material are completely water-filled, i.e. "saturated", whereas no moisture is present at the surface of the sample, i.e. "surface-dry". For a sample consisting of particles, such as sand or stone, the SSD state refers to the individual particles, i.e. the cavities in between the particles need to be empty whereas open porosities in each individual particle need to be water-filled. The assumed implication in this definition is that aggregate in its SSD condition will neither give off, nor take up water from cement paste – from a moisture point of view it can be considered "neutral" or at an "equilibrium point" – however, the situation is much more complex, for example:
- During cement hydration water from the aggregate pores may act as an internal curing agent and may have major implications for the hardened concrete properties [1]. That means, despite aggregate being added in its SSD state it is not "neutral", since water from its porosities may have major effects on the hardening and hardened concrete.
- Due to reduced packing of cement particles at the aggregate surface – formation of an interfacial transition zone in the cement paste with a higher w/c ratio – the surface of aggregate particles will require extra water to maintain an unaltered w/c ratio in the bulk paste. The finer the aggregate particle size, the more specific surface they will have, and the more significant this effect will be and will affect the water balance of the concrete.
- Aggregate particles with water-filled open pores, positioned in a heap, will for thermodynamic reasons at equilibrium necessarily also have water bound to the outer particle surfaces. This may be a negligible effect. However, for a heap of aggregate particles there will be interparticle, narrow porosities, including contact points, where there will be capillary bound water, and for fine particles this may be a significant effect. This is in conflict with the SSD definition which requires the individual particles to be both "saturated" and "surface-dry".

Identification of the SSD state
The look of an aggregate particles or another porous material may give information about its moisture state. When water is progressively removed from the material a series of visible changes will take place, though the distinctiveness of these will depend on the material color and texture:
- When the water content is so high that even the material surface is covered with a continuous, almost flat film of water, the material will appear dark and shiny reflective. The shiny appearance is due to reflection from the almost flat water-air interface, whereas the dark color is caused by reduced net reflection from the material surface due to internal reflections in the water film.
- At a lower water content the outer water film has an uneven surface due to menisci formation. This causes the surface to appear dull, diffuse reflective, whereas the dark color remains.
- At the lowest water contents the material will appear non-reflective and in a lighter color.
At the point where the material has just lost its outer water film it will be in the SSD state. This is a very simple method to establish the SSD state, and it will work for a broad range of particle sizes. However, it is also a very inaccurate method.

For coarse aggregate the suggested method by e.g. ASTM C127 [6] and EN 1097 [3] to establish the SSD state is initially to water saturate by immersion, and then subsequently remove surface water from the individual particles with an absorbent cloth. Obviously this method is not operational for fine aggregate and instead these standards prescribe use of a method, which may be referred to as the "cone method". Initially the aggregate is water saturated followed by slow and homogenous drying along with consecutive testing of samples for their free-flowing characteristics: A conical mold is filled with the aggregate particles, and at the point where the particle cone slumps, when the mold is removed, the sample is assumed to be in the SSD state. Fig. 1 shows the apparatus used for the cone method.
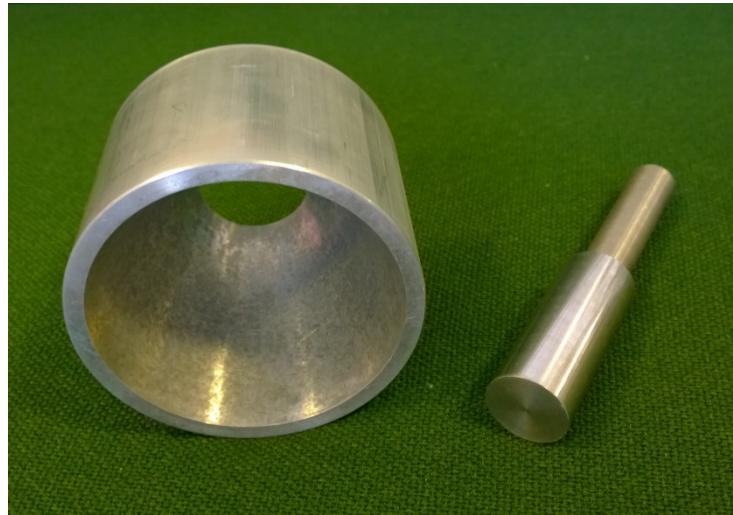
Fig. 1– Apparatus for determination of the saturated-surface-dry condition of fine aggregate according to ASTM C128 [7] and EN 1097 [3]. Left: Metal mold with internal cone shape, seen from the wide opening at the bottom. Height of mold is 75 mm. Right: Metal tamper to fill the metal mold.

For fine aggregate many other methods based on very different principles exist. However, common to these methods they are challenged when very fine particle fractions are present in the sample [3,7,8,9,10]. ASTM C128 [7] and EN 1097 [3] limit their use to particle sizes above 75 and 63 µm, respectively. If the sample contains particles smaller than 63 µm EN 1097 mentions that "this may affect the shape of the collapsed state.", but no suggestion is given as what to do. Even particles up to 150 µm size may pose problems in achieving the slump condition 10].

The ASTM C128 [7] and EN 1097 [3] have a notable difference in their SSD identification: According to ASTM the SSD state is reached when "slight slumping" is observed whereas according to EN 1097 the SSD state is beyond the point with "appreciable slump" and where an "almost complete collapse" has taken place "and slopes are angular". Fig. 2 shows examples of the slumped cone of sand close to the SSD state according to these definitions.

Fig. 2 – Sand tested according to ASTM C128 [7] and EN 1097 [3]. Photos are taken right after removal of the conical mold. Left: The moisture state is at a level where the complete particle cone has just achieved slump, i.e. no contours of the original cone shape exists. This is the SSD state according to ASTM C128. Right: The particle cone has slumped into the angular slopes required by the EN 1097 definition of the SSD state. Perhaps a tiny, slightly concave tip is still visible, indicating that the moisture state is just above the SSD state according to EN 1097.

Forces in action

The physical behavior of a group of filler or aggregate particles is the result of gravitational and electromagnetic interactions. Roughly speaking, for dry particles larger than 100 μm gravity is the dominant force. In a size range of 1-100 μm both the gravitational and the electromagnetic force may have relevance, whereas for particle sizes below 1 μm electromagnetic phenomena are dominant. When the particle system is wet, gravity may become a minor player even for particle sizes of a few mm [11,12,13].

The reason for the effect of particle size is the higher number of contact points and the related greater fraction of narrow size of cavities between fine particles compared with coarse particles. This enables intermolecular interactions – secondary chemical bonds, caused by electromagnetic forces – to play a role, in particular in the form of van der Waals solid-solid forces or in the form of liquid-liquid and liquid-solid hydrogen bonds generating capillary forces in liquid bridges between the discrete solid particles.

As an extreme example from nature, the ability of the gecko to climb vertical, perfectly smooth surfaces is due to van der Waals forces dominating gravity. In this case it happens even at a "particle size" (gecko size!) well beyond the rough size limits given above. Dry powders with particle sizes below 100 μm show the same phenomenon; Gravity may become less relevant as they cling to surfaces – adhesion – and they may exhibit a clumping behavior – cohesion – due to the individual grains sticking to one another by van der Walls forces.

The physical principle behind the ASTM and EN cone methods is that above the SSD state there will be interparticle capillary water present, which can overcome the gravitational pull and prevent the particle cone from slumping. When there is no interparticle water, gravity will bring a sand cone to slump. However, for dry filler the ASTM and EN particle cone may not slump at all when the mold is removed. In this case interparticle van der Waals forces are strong enough to overcome the gravitational pull. This prevents an identification of the SSD state of filler with the cone method.

To put it short, the cone method is based on an evaluation of capillary force vs gravitational force. For filler the limitation of the method relates to van der Waals forces being of similar magnitude as gravitational and capillary forces.

Suggested new method for SSD determination on filler

As demonstrated by the experiments described further on in this paper it is proposed to determine the SSD condition of filler by comparing the particle cohesion of frozen, molded filler samples. For samples with interparticle water the freezing markedly increases strength as the mobile liquid bridges of capillary water are changed to solid bridges of ice. Ice has a tensile strength in the order of size 0.7-3.1 MPa and a compressive strength of 5-25 MPa [14,15]. The single liquid bridge of capillary water is movable and will not carry compressive stresses and its tensile stress Δp at a meniscus radius, r, of e.g. 1 μm according to the Young-Laplace equation will be (Eq. 1):

$$(1) \qquad \Delta p = \frac{2\sigma \cdot \cos(\theta)}{r} \approx \frac{2\sigma}{r} = \frac{2 \cdot 72 \cdot 10^{-3} \frac{N}{m}}{1 \cdot 10^{-6}\ m} = 0.14\ \text{MPa}$$

Where σ is the surface tension of water and the approximation sign assumes near perfect wetting, i.e. contact angle, $\theta = 0°$. Obviously, the strength of a filler sample with a moisture content beyond the SSD state increases significantly on freezing.

EXPERIMENTS

Materials

Two materials were used for the experiments: 1) "Sand" from the location Øde Hastrup in Denmark. According to optical microscopy it consists mainly of quartz but it also contains porous and non-porous flint, calcite and fragments of granite. 2) "Alusilica" which is a by-product from the aluminium fluoride production [16]. The material sample has in a wet condition been pre-treated by the manufacturer with

CaO as to bind soluble fluorides. According to XRF and ^{29}Si and ^{27}Al MAS NMR spectroscopy the final dry product consists of 74.9 wt% amorphous SiO_2, 10.7 wt% CaF_2, 7.4 wt% $Ca(OH)_2$, and 7.0% $Al(OH)_3$.

Particle size characteristics of the two materials are given in Fig. 3. Based on SEM and EDAX mapping the alusilica consists of a huge number of homogenous, individual particles of typical sizes 1-5 µm, larger homogenous, individual particles which are relevant by mass, but not by number, and finally a considerable amount of clusters of these individual particles forming agglomerates which are difficult to break up [16], see Fig. 4.
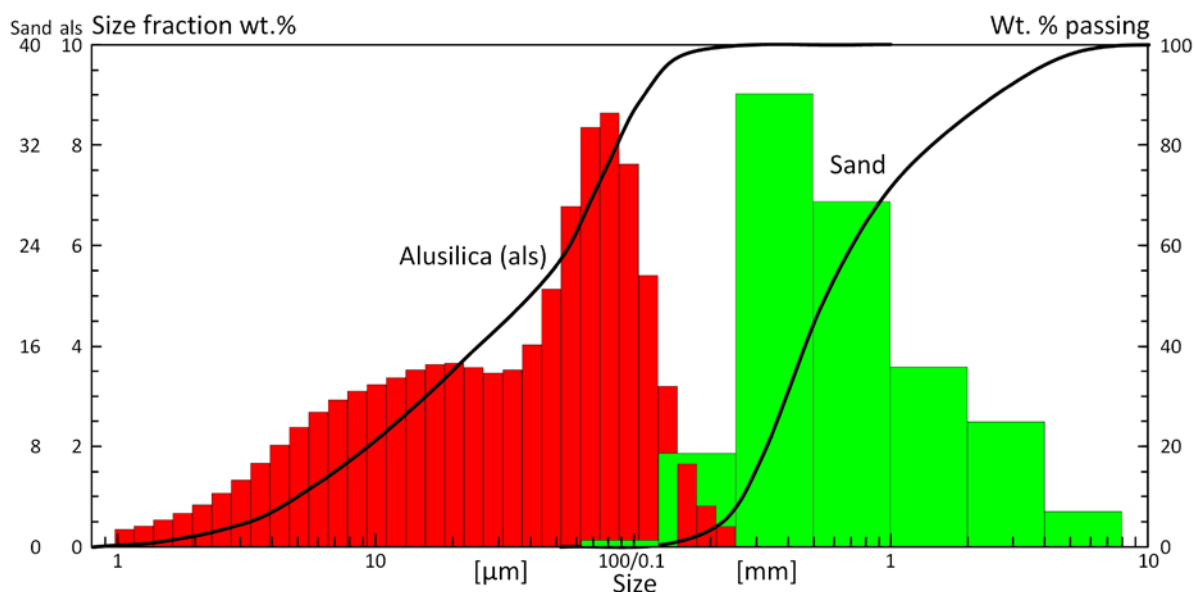

Fig. 3 – Particle size fractions (bars, left axis) and cumulative particle size distribution (lines, right axis) for alusilica and sand, measured by laser diffraction and sieving respectively. A large part of the alusilica consists of particle agglomerates. For this reason caution should be observed in the interpretation of the measured particle size distribution. Alusilica data are provided by the manufacturer.
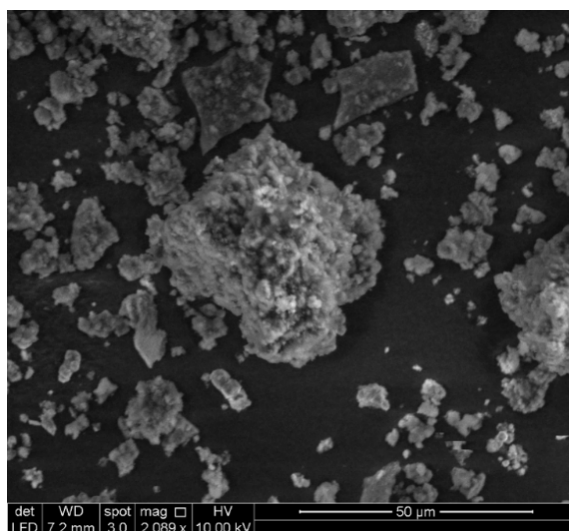

Fig. 4 – SEM image of alusilica. Scale bar is 50 µm. A 50 µm particle agglomerate is seen in the center surrounded by smaller agglomerates and individual, homogenous particles. From [16].

Due to its high content of amorphous SiO_2 the alusilica may potentially be used as a supplementary cementitious material for concrete. However, it has been observed that alusilica addition to concrete strongly affects the concrete flow properties [16]. A part of this influence may be explained by water absorption by the alusilica. Though the individual alusilica particle is dense and should not be able to absorb water, the alusilica agglomerates may have considerable porosities. It is, therefore, necessary to determine the water absorption of the alusilica.

Methods
Two methods were used to identify the SSD state of the alusilica and the sand: 1) The ASTM and EN cone method [3,7] and 2) a new method described below and referred to as the "freezing method". The present study was meant as a preliminary "proof of concept", not as a detailed study including identification of the limitations and uncertainties of the freezing method.

The new method initially follows the conditioning steps of the ASTM and EN methods. Firstly, the material is brought to complete saturation – storage under water for at least 24 h, perhaps aided by the use of vacuum. Next, the material is exposed to slow and homogenous drying. In the present experiments, instead of using a current of warm air (e.g. from a hair dryer) to evaporate surface moisture as described in EN 1097 the material was gently heated on a frying pan with continuous stirring to keep the moisture state homogenous throughout the material. It was the concern that drying with a hair dryer in some case might remove the very fine particles. The heating was stopped at regular intervals (e.g. 5 minutes) and the material was allowed to cool down whilst further stirring the sample. This was done to consecutively lower moisture contents, and at each moisture content a sample was taken and analysis was done.

At this point the freezing method deviates from the standard method; instead of testing cone slump at the various moisture contents cylindrical plastic tubes were filled with the material, see Fig. 5.

Fig. 5 – PTFE tubes with an internal diameter of Ø14 mm and length 150 mm. The tubes were filled with the particulate sample and closed with rubber bungs in both ends.

It was attempted to fill the tubes in a homogenous and reasonably reproducible way, similar to packing methods described in ASTM C29 [17] and EN 1097 [3]. Non-absorptive PTFE tubes, length 150 mm with an inner opening of Ø14 mm, were filled in 4 layers where each layer was lightly tamped 15 times with an Ø10 mm glass rod. The tamping was just strong enough to remove coarse cavities, but not so strong that it would generate considerable compaction of the particle system.

After filling the tubes, the samples were transferred to a standard household freezer at -18°C. They were kept there for at least 1 day to ensure freezing of their contained water. The samples were then brought to a walk-in freezer at -5°C and demolded into petri dishes with a pneumatically driven piston. The reason for demolding in a walk-in freezer was only for the sake of being able to carry out an extended examination of the samples, including taking photographs in the frozen condition. The thermal inertia of the samples would allow sufficient time for examination of the samples at room temperature. Finally, the petri dishes with particulate material were dried out at 105°C. Based on the mass change during drying and the dried material mass, the moisture content of each sample was subsequently calculated.

RESULTS AND DISCUSSION

In total approximately 100 samples of sand and alusilica were prepared for the freezing method in addition to a series of ASTM and EN cone tests at different moisture contents. Five independent operators were involved as to examine both repeatability and reproducibility of the methods. For all methods – ASTM, EN and freezing method – it seemed clear that the most important factor in increasing the accuracy is a few repetitions of the experiments. Additionally, it seems important that the operator has experience in the test methods, by trying it a few times before "real" measurements are done, but apart from this, the operator dependence, i.e. reproducibility, has less relevance than repeatability. Some further information on this can be found in [18].

Cone method

Initial experiments showed as expected that the cone method cannot be used for the alusilica due to its fine particle size. As seen in Fig. 6 no slump is observed even though the sample is in an almost oven dry condition. Due to the fine particle size there will be a high number of particle contact points allowing van der Waals forces to prevent gravity from disintegrating the particle cone. A similar examination of the sand with the cone method does not display the same problem as for the alusilica, see Fig. 7. The cone method would also not be operational for <63 µm particles based on the sand [18].
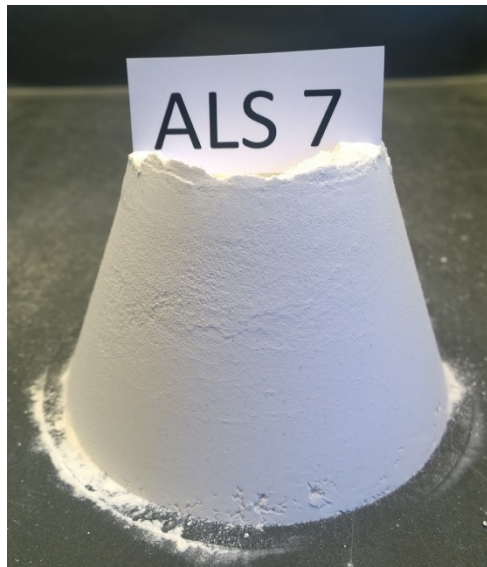

Fig. 6 – Alusilica tested with the cone method. The moisture content is 1.0% – much below the SSD condition (approx. 14.0% as shown later). However due to electromagnetic forces the sample completely retains the shape of the mold when it is removed – as seen it was even possible to position a sample marker without inducing slump of the cone.

ASTM C128 and EN 1097 tests on the sand results in a SSD moisture state of (1.4±0.1)% and (0.6±0.4)% respectively. The higher value given by ASTM compared with EN is expected, cf. the description in the "Background and concept" section. The higher uncertainty on the EN value is also

expected since it is more difficult to identify when the collapsed cone has a "definite peak" and its "slopes are angular" as required by the EN standard. This difficulty is indicated in Fig. 2, and we have previously done several hundred of EN 1097 SSD determinations substantiating this difficulty. Measurement accuracy related to ASTM C128 is treated for example in [19].

Fig. 7 – Sand tested with the cone method. Left: Moisture content u=3.0%, where menisci formation in the interparticle water generates cohesive forces – "interstitial liquid bridges" – between the sand particles and retains the shape despite removal of the mold. Right: Moisture content u=0.3%, where the moisture content is below the SSD state. Due to absence of sufficiently strong interparticle forces, in this case notably absence of interparticle water, the sample slumps completely when the mold is removed.

Freezing method

Samples produced according to the freezing method could be classified in two distinct groups on demolding. The demolded samples of alusilica and sand appeared either as individual particles or as a solid mass, in a rod shape from the molds, though they during demolding and handling might break in a couple of pieces. Fig. 8 shows examples of demolded sand samples near the SSD state, where the solid to particle transformation should take place. Fig. 9 shows alusilica samples near the SSD state.

The same situation applied to the alusilica except from this materials not being free-flowing, i.e. it could not be poured out of the mold even in the dry state. But after demoulding of alusilica it appeared either in a distinct cohesive state, i.e. rod-like, or in a non-cohesive, i.e. powderous state.

Based on measurements with the freezing method the SSD moisture content was determined to be (1.7±0.1)% for the sand and (14.0±1.0)% for the alusilica. Based on the sand measurements, it seems that the freezing method gives values in accordance with, but slightly higher than the ASTM method, whereas the EN method exhibits some deviation from these two.

From the experiments it seems that the freezing method is capable in determining the SSD moisture level of both sand and fillers. Additionally, this method seems to identify the SSD moisture level in a more distinct way than can be done with the ASTM and EN cone method. On the other hand it takes longer time to get the measuring results with the freezing method – 2-3 days instead of 1-2 days (saturation, testing, measuring moisture content). For both methods the needed instrumentation is very simple.

The freezing method presented here may potentially be improved in several ways, including the mold system and the cohesiveness test of the samples after demolding. It may be possible to develop the method into a standard test.
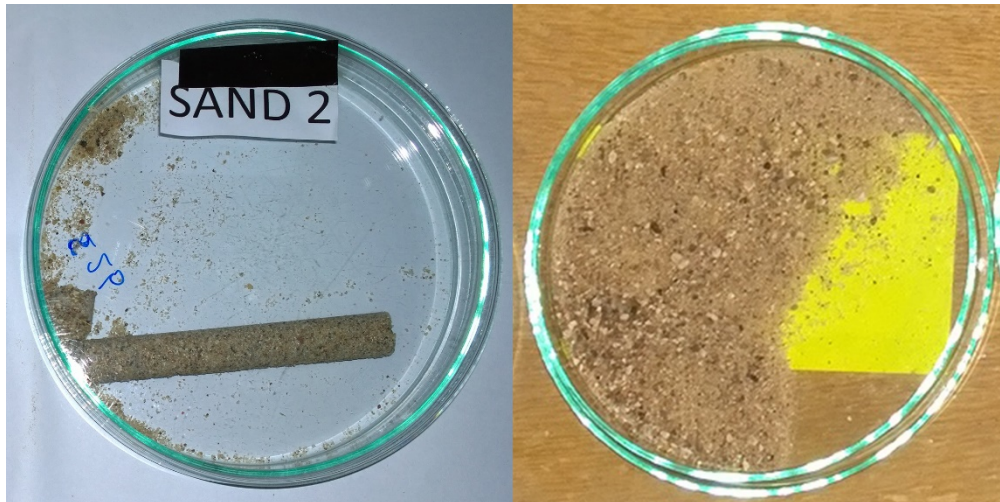
Fig. 8 – Frozen sand samples after demolding. Left: Moisture content u=3.0%, where the sample has considerable strength with notable particle cohesion. Right: Moisture content u=1.3%, where there is apparently no particle cohesion and the sample comes out from the mold as individual particles.

Fig. 9 – Frozen alusilica samples after demolding. Left: Moisture content u=16.6%, where the sample has considerable strength with notable particle cohesion. Right: Moisture content u=12.4%, where the sample disintegrates into powder during demolding – the small pieces seen have no relevant cohesion and disintegrate at the slightest touch.

CONCLUSIONS

A new method – "freezing method" – for identifying the SSD state of materials with particle sizes below approx. 100 µm – "fillers" – is suggested. In this particle size range the standard ASTM and EN test methods are not operational. For sand the freezing method seems to give results which are close to the ASTM test methods. With the freezing method SSD moisture content of a filler "alusilica" has been successfully determined. Potentially the presented new technique may be established as a standard, but it will need to be examined further.

The method of using freezing was proposed – in lack of better – by the present author to his students R.S.Bundgaard and S.S.Kjær during their BSc project [20]. Their promising test of the technique initiated the present report. In addition to the author's own measurements, further experimental results from the BSc work of A.E.A. Nielsen and C.H. Hansen [18] have been included here as to update and revise a previous version of the present paper [21].

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