Study of Diatomaceous Earth as a Soil Additive for Improving the Water Retention of Lawn Toplayers

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1. Introduction

There are at least 42,000 turf sport grounds[3] [1,2] and 693 golf courses (German Golf Association, 2008) [3] in Germany. To guarantee that these facilities can be played on all year round, there are special requirements for the soil. One is that water permeability is provided for, for example, by sandy or gravelly layers and ditches for drainage. As a consequence of such a build-up, an increased amount of sprinkling during dry periods is to be expected [4].

To lower the amount of sprinkling, one possibility is to improve the water-retention capability of the lawn base layer. A multitude of inorganic additives can be used to do this, Examples of such are expanded clay, diatomaceous earth and zeolites [5]. All these products promise an improvement in the lawn base layer and are approved according to the rules of the USGA (United States Golf Association) [6,7]

The fossilised, mineral remains of diatoms are called diatomaceous earth. These are microscopically small, amorphous silicified skeletons with low bulk density (1 cm of diatomaceous earth contains approx 1 billion diatom skeletons or fragments of such).

Diatoms are single-cell microorganisms, which primarily live in fresh water, brackish water or seawater. Some species, however, are also found on land. Diatoms are the main constituent of phytoplankton in the seas, thus constituting a substantial part of the marine food chain.

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3) Based on the number of football clubs [2] and the turf sport grounds available to them in Bavaria [1], this was extrapolated for the total number of football clubs in Germany.

When they die, their silicate skeletons sink undamaged to the seafloor where they form sediments of diatomaceous earth beneath the calcite compensation depth. These deposits can be up to several hundred metres. The sights of such deposits come to the surface as a result of shifting or drying. [8].

Untreated diatomaceous earth consists for the most part of silicon dioxide. This may have impurities of up to 10% inorganic components (e.g. alumina, calcium carbonate, sand and iron oxides) and up to 35% organic components. The amount involved in the purification process depends on the deposit site and the technical application. Diatomaceous earth is used in many production processes and products. Classic areas of application are filter material, fillers in thermal insulation, building materials, coatings, sanding and polishing materials, in animal feed and as a carrier for fertilisers, pesticides and insecticides [9].

Deposits sites are found all around the world. Thus in 2005 roughly 2.02 million tons of diatomaceous earth were mined, the main production countries having been the USA, (653,000 t), China (410,000 t), Denmark (234,000 t) and Japan (130,000 t). The organic components are removed by firing, during which the diatoms vitrify into larger agglomerates, without losing their porosity, however. If the firing is done at very high temperatures, crystallisation may come about. Typical products then produced are: quartz, cristobalite and tridymite. Thus it is necessary to avoid crystallisation, because crystalline diatomaceous earth with grain sizes less than 5 µm can trigger silicosis [9].

The following paper gives the results of some soil-physics studies and material-characteristics studies of fired and unfired diatomaceous earth.

The samples of diatomaceous earth were procured by Consagros GmbH & Co and come from the following deposit sites: Queensland (Australia), Fünen (Denmark) and Nevada (USA). The only untreated starting material available was the diatomaceous earth from Nevada. The samples from Australia and Denmark were only fired diatomaceous earth.

2. Examinations

Materials-science studies of the samples of diatomaceous earth were carried out by the University of Augsburg at the Chair of Solid Body Chemistry. The soil-physics studies were carried out at the Georg Armbruster Soil Laboratory (within the framework of a Bachelor of Science thesis). The macro-pore analysis was carried out by Quantachrome in Odelshausen in accordance with DIN 66133. The element analysis was drawn up by Bifa GmbH environmental Institute (Bavarian Institute of Applied Environmental Research and Applied Technology) in accordance with DIN EN ISO 11885 and DIN ISO EN 11969.

2.1 Morphological examinations

Structure and porosity are important material characteristics, which explain the physical characteristics of diatomaceous earth. To do this, scanning electron microscopy (SED) images are made and the total pore distribution is determined by means of mercury porosimetry. Using the SED, the samples were examined for their external morphology. Figure 1 shows the open-pore structure of a diatom fragment, the pore diameter of which, however, is unsuitable due to its diameter being too small for plants. Water stored in pores smaller than 0.2 µm in diameter is then not accessible to plants.
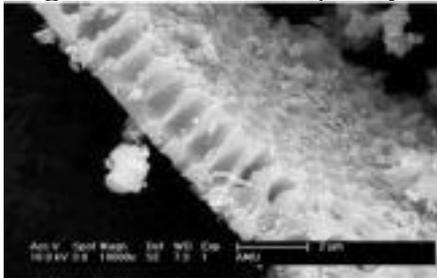
Fig. 1: SED image of a diatom fragment

Fig. 2: SED image of an intact quartz skeleton of a diatom cell
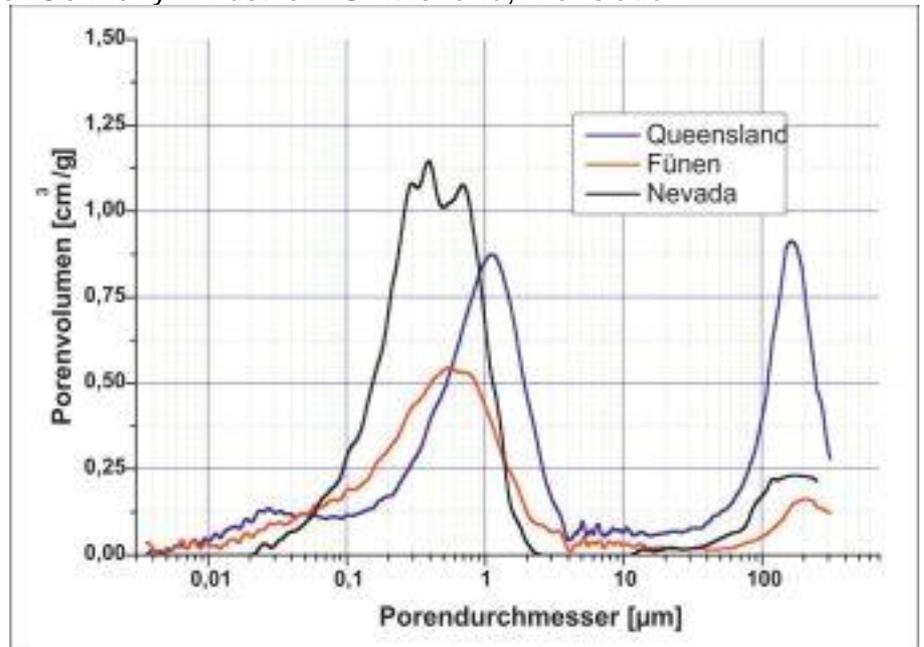
Fig. 3: Pore size distribution of diatomaceous earth, determined by means of mercury porosimetry

Porenvolumen = Pore volume

Porendurchmesser = Pore diameter

Figure 2 shows an intact silicate skeleton of a diatom cell.

In spite of vitrification with other diatom fragments, a hollow body with a medium pore (about 4.5 µm) remains. Water retained in these is accessible to plants.

Microscopic examinations only render the surface structures, but the total porosity is an important indicator of the water-retention capability.

For this reason the total pores are determined by means of mercury porosimetry. Figure 3 describes the first derivation of the pore size distribution in a logarhythmic plot. Between 40 µm and 300 µm is the so-called intergranular volume, which depends on how fine the

Deposit site	Integration limits	Pore volume
Queensland	0.2 µm - 10 µm	0.64 cm^3/g
Fünen	0.2 µm - 10 µm	0.45 cm^3/g
Nevada	0.2 µm - 10 µm	0.78 cm^3/g

Table 1: Pore volume per gram of diatomaceous earth within a range of 0.2 - 10 µm

granularity of the sample is. The so-called medium-porerange is between 0.2 and 10 µm (equivalent to the pF range 2.4-4.2). Additional water retained there can be used by plants. The pore volume was therefore set within limits of 0.2 and 10 µm. The results are shown in Table 1.

2.2 Thermal analysis

The manufacturing process (firing of diatomaceous earth) was examined more closely using thermal analysis. The firing process of the diatomaceous earth is simulated in a thermo balance coupled to a mass spectrometer (capillary coupling). This type of coupling splits up the mass signals better. Figure 4 shows the mass change and the temperature against the time, and simultaneously the main masses of water (mass 18 t[m/z]) and carbon dioxide (mass 44 [m/t]) are measured. The firing process can be described as follows: First dehydration in several partial steps, followed by a seamless transition to the firing of the organic residues (water and carbon dioxide (CO_2) are released), followed by decarbonisation of inorganic components.
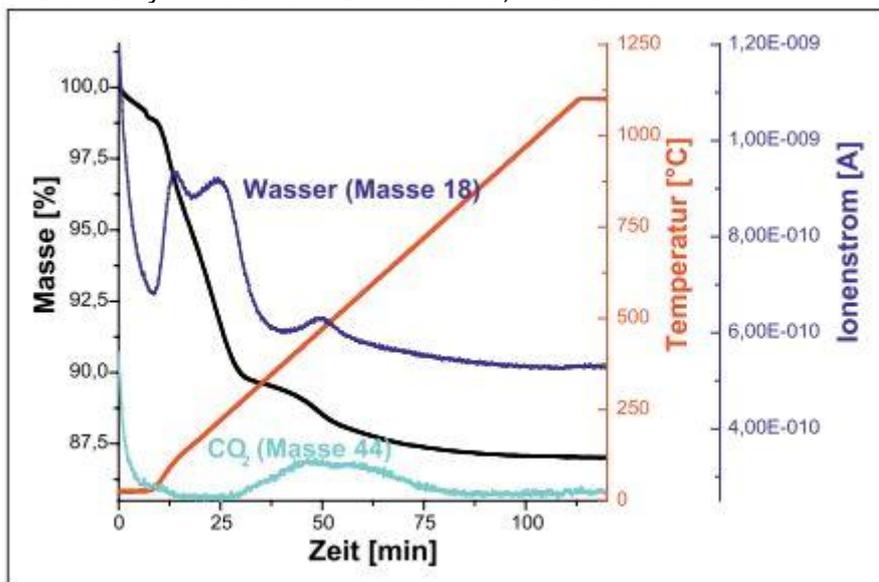
Fig. 4: A change in mass during firing of diatomaceous earth (Nevada) and simultaneous detection by means of capillary coupling of the gases being released (mass 44 [m/t] was scaled up for better portrayal by a factor of 10).

Zeit = Time

Masse = Mass

Ionenstrom = Ionic current

Temperatur = Temperature

Wasser = Water

The relatively low decomposition temperature (550° C) of the inorganic carbonates along with the results of the element analysis suggest magnesium carbonate.

To achieve higher sensitivity of the mass detection, the measurement was repeated on askimmer coupling. When this is done the gases being released are put into the mass spectrometer coupled at a higher concentration. At approx 700° C, SO2 is also released from the sulphate decomposition (Fig. 5). The decomposition temperature and the results of the element analysis suggest magnesium sulphate.
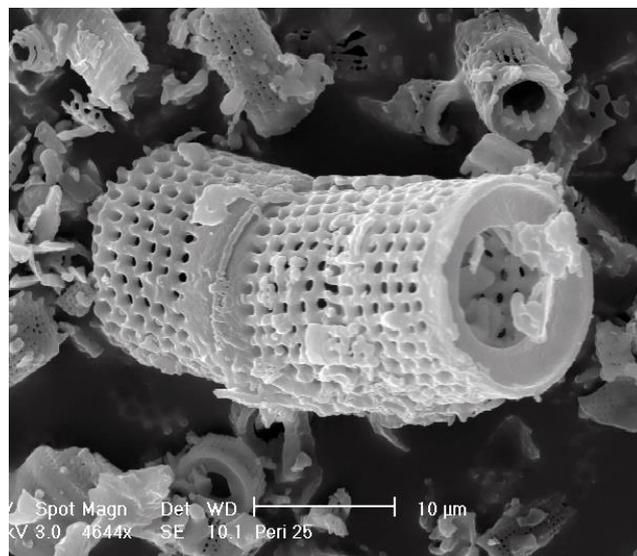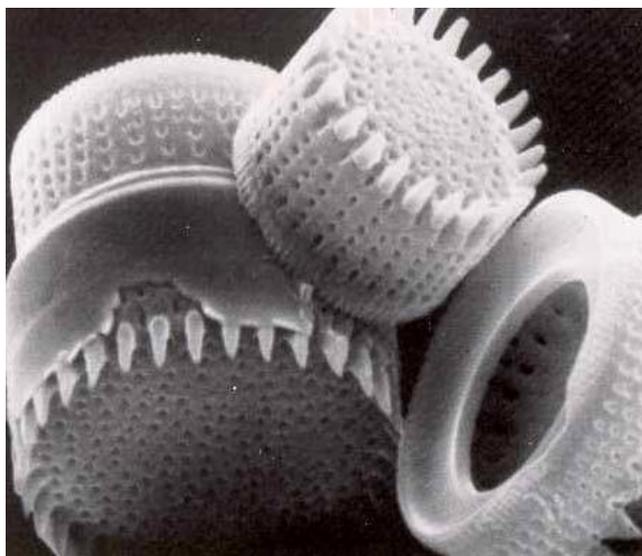
2.3 Structural examinations

Structural examinations of the diatomaceous earth explain its physical and chemical properties. For this reason the diatomaceous earth was measured by powder x-ray diffraction and compared with the JCPDS (Joint Committee for Powder Diffraction Standards) database.

The crystalline areas of the three samples differed from one another in part substantially. This may be attributable to the quality of the mining sites. Quartz and iron oxide (Fe_2O_3) can be matched up to the diatomaceous earth from Fünen. In the Queensland sample iron oxide can only be inferred with the aid of the EDX data (Section 2.4). The sample from Nevada is nearly X-ray-amorphous (Fig. 6). If diatomaceous earth is fired too long or too high, quartz and cristobalite develops (Fig. 7)
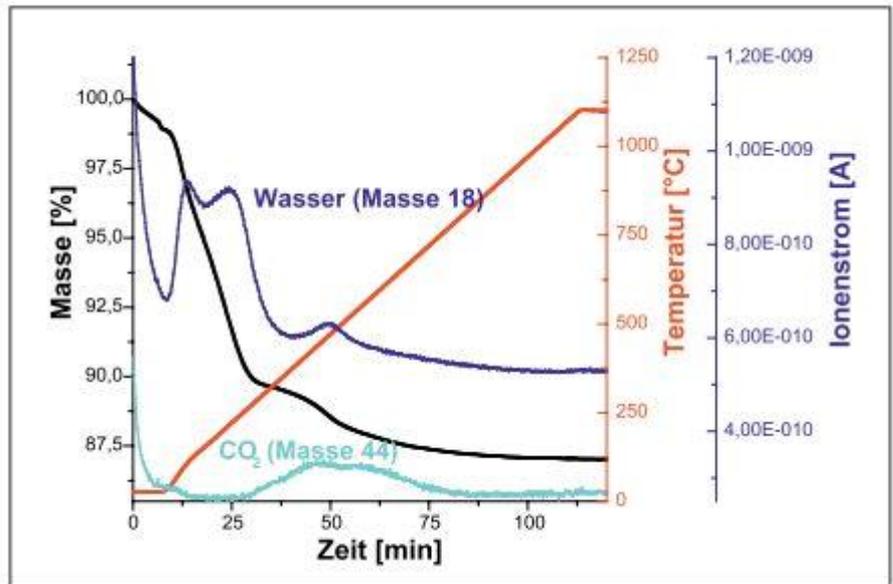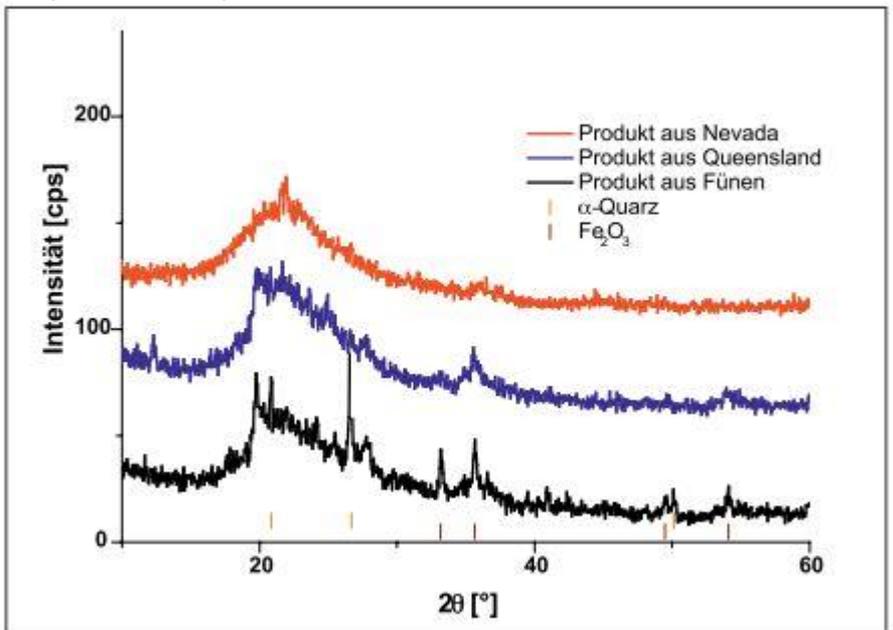

Fig. 5: The change in mass when diatomaceous earth (Nevada) is fired and simultaneous detection of the gases being released by means of skimmer coupling.

Zeit = Time; *Masse* = Mass; *Ionenstrom* = Ionic current; *Wasser* = Water
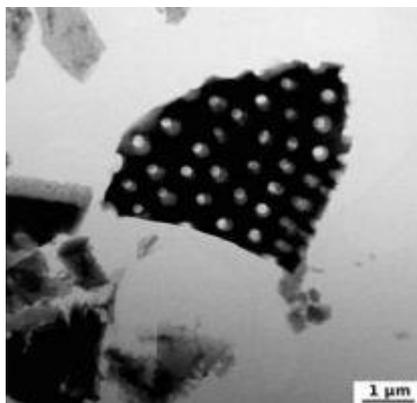*Temperatur* = Temperature
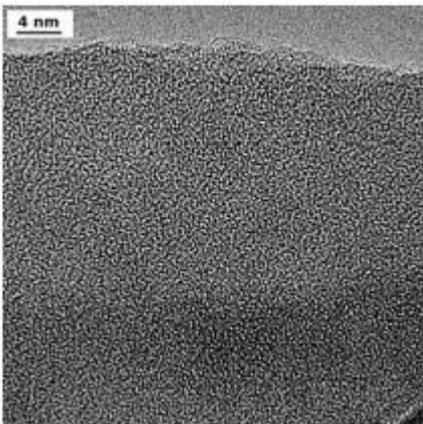
Fig. 8: HRTEM Image (picture) of the diatomaceous earth from Nevada

Fig. 9: TEM image (picture) of the diatomaceous earth from Nevada

Fig. 6: Powder x-ray diffractogram of samples of diatomaceous earth. For a better overview the measurements on the y-axis were shifted upwards by 50 cps (counts per second) in each instance. The coloured marks indicate the reflex positions of the phases (connection) based on the JCPDS database.

Intensität = Intensity; *Produkt aus* = Product from

The main reflex of cristobalite forms after a 12-hour heating period at 1000° C. But if heating is carried out for 12 hours at 1100° C, in addition to cristobalite, Fe_2O_3 and quartz are also formed (Fig. 7). Another aid in structural analysis is high-resolution transmission electron microscopy (HRTEM). These examinations confirm the amorphous structure of the diatomaceous earth from Nevada (Fig. 8).

Transmission electron microscopy (TEM) once again shows the open-pore structure of the diatomaceous earth (Fig. 9).

2.4 Element composition

An analysis unit installed on an electron microscope allows element composition to be determined by means of EDX (energy dispersive X-ray). Figure 10 shows a freely scaled energy spectrum in the example of the diatomaceous earth from Nevada.

Table 2, which goes with it, lists the elements detected in mass percent (as metal oxides).

Since an EDX measurement only determines the concentration of the elements in the percent range, the samples were also supplemented for their heavy metal contents by means of atomic emission spectroscopy (ICP - OES) in accordance with DIN EN ISO 11885 and atomic absorption spectroscopy (AAS) in accordance with DIN EN ISO 11969. An excerpt of these results is listed in Table 3.

The German Sewage Sludge Act may be consulted to assess the heavy metal concentrations [10]. According to it:

"Applying sewage sludge to ground used for agricultural or gardening purposes is prohibited if sewage sludge examinations as per Section 3, Para. 5, show that the contents of the following heavy metals exceed at least one of the following values (milligram per kilogram of sludge dry mass)":

The heavy-metal concentrations fall short of the limits required to a great extent. The detection limit for cadmium is 40 mg/kg and therefore outside the specification. The content of mercury was not determined. An addition of or re-examination for the two heavy metals should therefore be carried out.

2.5 Soil-physics examinations

The following soil physics examinations were in part limited to the diatomaceous earth from Nevada. The examinations were carried out on the fired diatomaceous earth from Nevada, a mixture of 10% by volume of diatomaceous earth (Nevada) in quartz sand (granulation size 0-2 mm) and pure quartz sand.

### 2.5.1 Determination of the grain distribution

The grain distributions of the quartz sand mixture (diatomaceous earth from Nevada) and the pure quartz sand run nearly the same. According to DIN 18035-4, grain distribution within the particle-size distribution curve is called for for lawn base layers and therefore, when used in lawn base layers, should be additionally mixed with a topsoil rich in fine grain. Of prime importance, however, is the comparison between quartz sand and quartz sand/diatomaceous earth, for which reason no correction of the grain distribution has been made.
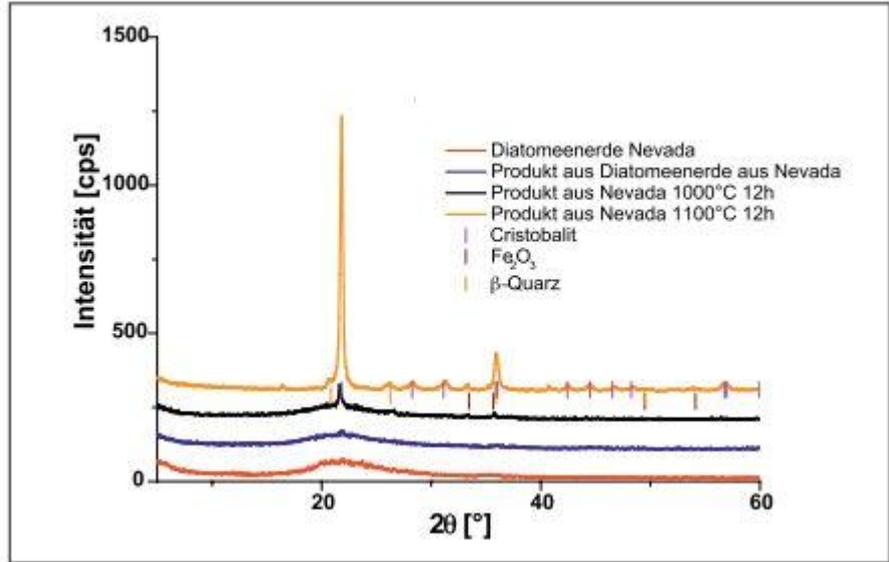
Fig. 7: Powder x-ray diffractogram of thermally treated diatomaceous earth from Nevada. For a better overview the measurements on the y-axis were shifted upwards by 100 cps (counts per second) in each instance. The coloured marks indicate the reflex positions of the phases (connection) based on the JCPDS database.

Intensität = Intensity; *Diatomeenerde* = Diatomaceous earth; P*rodukt au*s = Product from; *Cristobalit* = Cristobalite
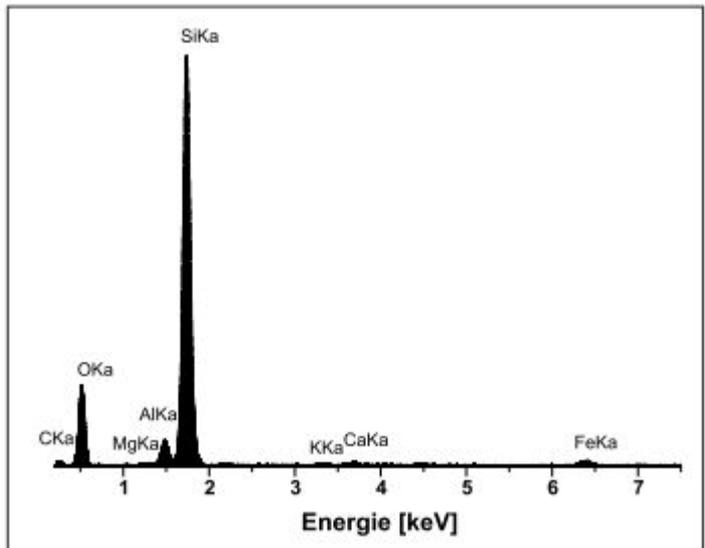
Energie = Energy

Fig. 10: Freely scaled energy spectrum of the diatomaceous earth from Nevada

Percent by mass	Queensland	Fünen	Nevada
SiO$_2$	81.87	74.85	85.58
Fe$_2$O$_3$	9.10	5.04	3.06
Al$_2$O$_3$	8.03	12.06	9.56
CaO	–	0.65	0.68
MgO	1.00	2.93	0.68
K2O	–	1.44	0.44
Na$_2$O	–	1.29	–
TiO$_2$	–	1.74	–

2.5.2 Determination of the Proctor density

Unfortunately, the Proctor density of the diatomaceous earth from Nevada could only be determined to a moderate degree, for which reason no account will be given. One reason for this could be the extremely large water-retention capability of the diatomaceous earth, which does not allow exact determination of the Proctor density with optimum water content.

Comparing pure quartz sand with quartz-sand mixture, however, one identifies a doubling in the optimum Proctor water content from 8% to 17.5% (Fig. 12).

2.5.3 Determination of the retention curve

To determine the retention curve (DIN 18125) the samples were first compacted to 0.95 _pr. Measuring was done at pF 1.8 (wide coarse pores), pF 2.5 (narrow coarse pores), pF 3.6 (medium pores, the required pF value of 4.2 for determining the total medium-pore range not having been possible with the testing apparatus used) and pF 7 (fine pores, drainage at 105 °C).

The fraction of medium pores for the quartz-sand mixture correlates very well with the individual measurements (5.1%), but at 11.2% the fraction of fine pores is above the expected 9.6%. Figure 13 describes the retention curve and Table 5 does so for the percentile pore volumes of the fine- and medium-pore ranges.

2.5.4 Determination of the water absorption capacity according to Enslin-Neff

A dry soils' suction and holding force by capillary action is called water absorption capacity [11]. When the sample was prepared, it was not ground so as not to destroy the pore structure. The equilibrium state developed in two hours. The increases in mass are listed in Table 6.

Massenanteile der Körner < d in % der Gesamtmenge = Mass fractions of the grains < d in % of the total amount

Schlämmkorn = Washed particle;

Schluffkorn = Silt grain

Ton = Clay *Fein*

= Fine *Mittel* =

Medium

Grob = Coarse

Siebkorn = Sieving grain

Sandkorn = Sand grain

Mass in g/kg	Queensland	Fünen	Nevada
Arsenic	0.01	0.01	0.01
Lead	<0.07	<0.07	<0.07
Cadmium	<0.04	<0.04	<0.04
Chrome	<0.04	<0.04	<0.04
Copper	<0.04	0.13	<0.04
Nickel	<0.04	<0.04	<0.04
Mercury	not determined	not determined	not determined
Zinc	0.22	0.11	0.06

Table 3: Heavy-metal concentrations of the diatom samples

2.5.5 Determination of the field capacity

The samples were compacted to 0.95 _pr and flooded with water for 24 hrs. Afterwards the mass was determined and reweighed after two hours' drainage time. The diatomaceous earth from Nevada has a field capacity of 150.4 M.-%. The quartz sand mixture shows an improvement of approximately 2.5% compared with pure quartz sand, which is much less than the increase of 11% to be expected by calculation (Fig. 14).

2.5.6 Determination of the laboratory capacity (LK 100)

The sample bodies had a degree of compaction of 0.95 and were dried before the start of testing (105° C to constant weight) and then left in the testing apparatus for 48 hours. The quartz sand mixture shows a 32.5% increase in comparison with pure quartz sand (Fig. 14). Mathematically, a 41% increase would expected.

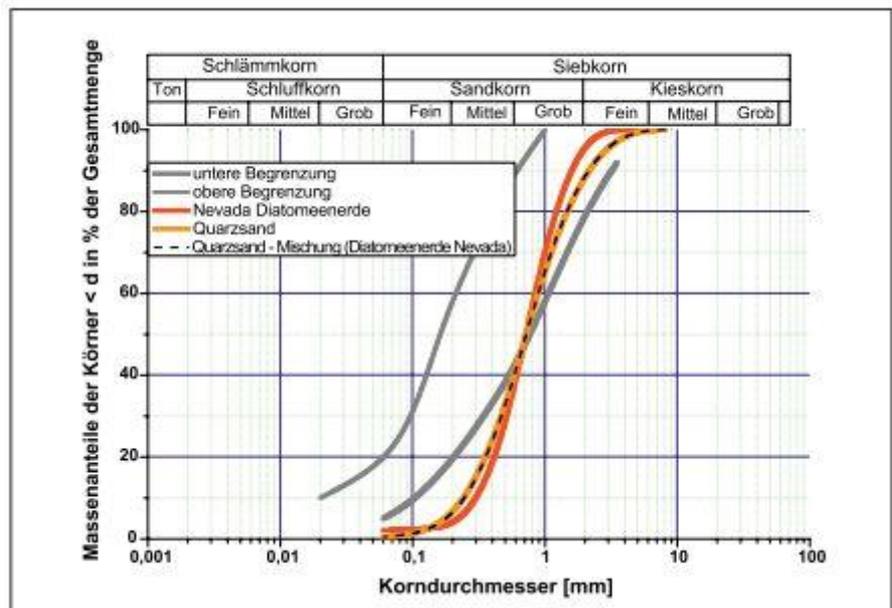| Lead	900 *
Cadmium	10
Chrome	900
Copper	800
Nickel	200
Mercury	8
Zinc	2500
(* mg/kg)"4	

untere Begrenzung = Lower limit

obere Begrenzung = Upper limit

Nevada Diatomeenerde = Nevada diatomaceous earth

Quarzsand = Quartz sand

Quarzsand - Mischung (Diatomeenerde Nevada) = Quartz-sand mixture (diatomaceous earth from Nevada)

Korndurchmesser = Grain diameter

Fig. 11: Comparison of grain size distribution (DIN 18123). The samples for quartz sand and quartz-sand mixture (diatomaceous earth from Nevada) overlap.

3. Discussion

The samples of diatomaceous earth differ very much from one another in the medium-pore range from 0.2 μm - 10 μm. The pore volumes vary between 0.45 and 0.78 litres per kg of diatomaceous earth (see 2.1 mercury porosimetry).

A further quality criterion is the mineral composition of the samples. The powder x-ray diffractograms in conjunction with the element analysis make clear the differences in the composition of the products. All the diatomaceous earth samples are free of cristobalite, tridymite and quartz. This suggest good processing (gentle firing).

The water absorption capacity of the fired diatomaceous earth samples, determined according to Enslin – Neff, varies between 93.3 and 125% by weight. The pore volume determined by means of mercury porosimetry (within the limits of 0.01-50 μm) differs by about 20% downward. It is conceivable that pore material was destroyed by the measuring method of mercury porosimetry (introducing mercury into the sample under high pressure).

The determination of the Proctor density shows more than a doubling of the water content (8% quartz sand compared with 17.5% quartz-sand mixture). To determine the retention curve, laboratory capacity and field capacity, the samples were compacted to 0.95 pr. The retention curve describes the distribution of the pores with a Proctor density of 0.95 ρ_{pr}.

The improvement in the quartz sand mixture correlates well with the increase in medium pores to be expected mathematically. At the same time, however, the fine-pore fraction in the quartz-sand mixture increases by about 12%.

The laboratory capacity, i.e. the suction by capillary action of the soil matrix and thus the holding power against gravity, of the quartz-sand mixture shows a 32% improvement compared with quartz sand. This value is somewhat below the expected improvement of 41% The mathematical water content can be
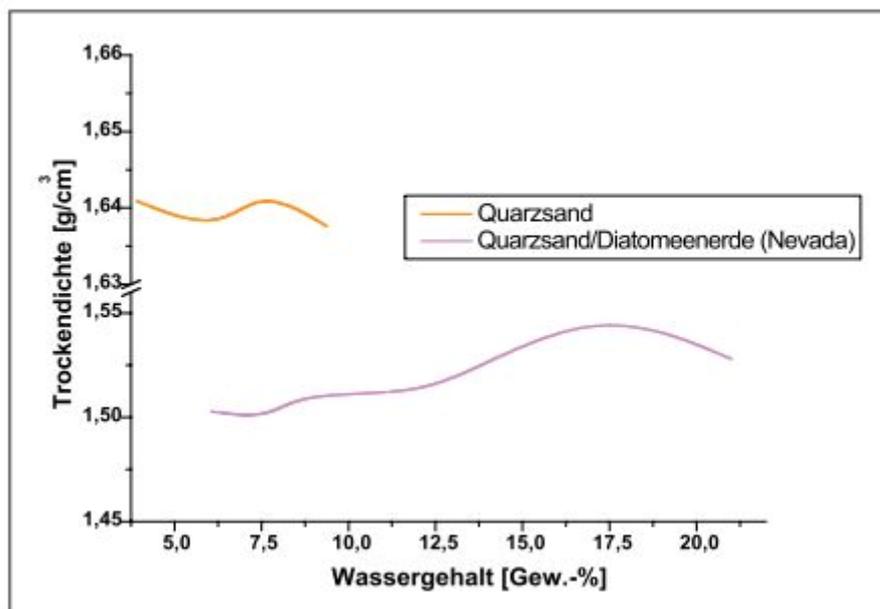
Fig. 12: Comparison of the Proctor density of quartz sand and quartz sand/ diatomaceous earth (Nevada)

Trockendichte = Dry density
Wassergehalt = Water content

Quarzsand = Quartz sand
Quarzsand/Diatomeenerde (Nevada) = Quarzsand/diatomaceous earth (Nevada)
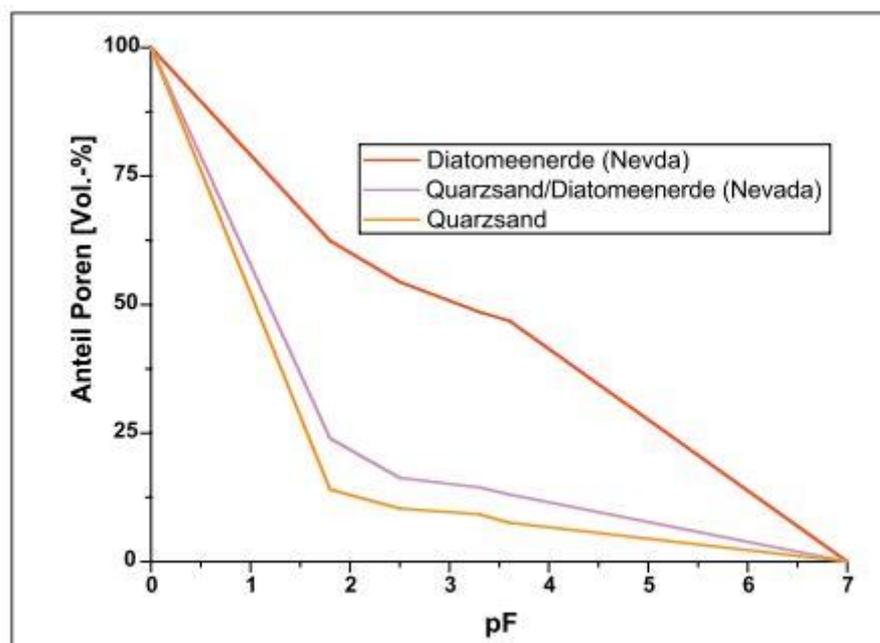
Fig. 13: Retention curve (pF test, DIN 18125)

Anteil Poren [Vol.-%] = Fraction of pores [% by vol.]

Table 5: Breakdown of the fine and medium pores in percent by vol.

Diatomaceous earth	Australia	Fünen	Nevada
	93.3%	98.8%	125%

Table 6: Water absorption capacity in percent according to Enslin-Neff

The field capacity measurements show an improvement in the quartz-sand mixture compared with pure quartz sand. At 2.5%, the increase in the field capacity, however, turns out less than the expected 11%.

With the Proctor density of the diatomaceous earth adjusted incorrectly, the water contents of the laboratory capacity and field capacity ascertained could turn out to be too high. This could explain the water contents of the quartz-sand mixture with laboratory capacity and field capacity not being reached mathematically.

4. Summary

@g:All three samples of diatomaceous earth display a large medium-pore range, which is ideal in terms of storing water and its availability to plants. The measurements of the retention curve, field capacity and laboratory capacity reveal in part a non-linear relationship between diatomaceous earth and the quartz-sand mixture. Thus the field capacity and laboratory capacity turn out less
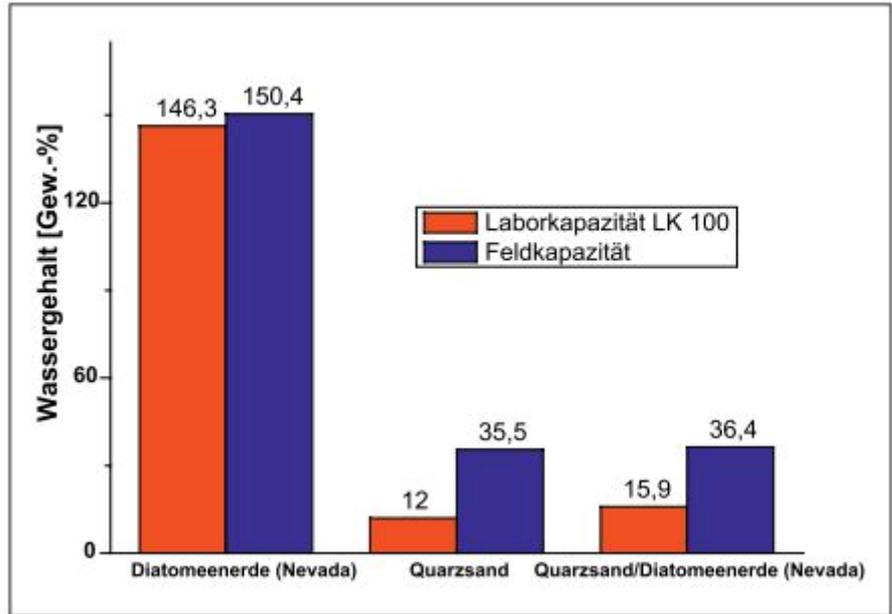

Fig. 14: Graphic comparison of the laboratory capacity and field capacity

Wassergehalt [Gew.-%] = Water content [% by weight]

Laborkapazität = Laboratory capacity

Feldkapazität = Field capacity

Since water as a raw material is gaining ever more in economic and ecological significance, ways to

Diatomeenerde (Nevada) = Diatomaceous earth (Nevada)

Quarzsand/Diatomeenerde (Nevada) = Quartz sand/Diatomaceous earth (Nevada)

than expected mathematically. This, however, could be due to the Proctor density of the diatomaceous earth being very difficult to determine. The increase in the medium pores, according to the retention curve, correlates well with the values expected. At the same time, however, the fine-pore fraction of the quartz-sand mixture increases by about 12%.

save it must be reflected upon. The soil-physics properties of the quartz-sand mixtures (with regard to laboratory capacity and field capacity) may not behave in a linear fashion, but an improvement compared to pure quartz sand is in fact identifiable. Adding 10% diatomaceous earth to the lawn base layer would therefore be a worthwhile supplement to existing water management systems.