

## COMPARISON OF THE TRADITIONAL ENSLIN-NEFF METHOD AND THE MODIFIED DIENG METHOD FOR MEASURING WATER-UPTAKE CAPACITY

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**Abstract**—A method for the determination of the water-uptake capacity of powders which is said to be applicable to viscose silk, specific celluloses, soap, paint, glue, gelatine, adhesives based on starch, biological samples, and soils, was proposed by Enslin in 1933 and has been improved several times since then. Today in Germany, the so-called Enslin-Neff method is used by the clay industry, in civil engineering, and in soil science. Many authors have identified the influence of evaporation on the results obtained using this method and the latest modification of the Enslin-Neff method was introduced by Dieng in 2005 where a balance was used instead of a burette to record the water-uptake capacity. It is proved here that the Dieng method actually operates correctly, independent of relative humidity. Therefore, a significantly improved reproducibility of the Dieng method compared to the traditional method was expected. However, it was found that the Dieng apparatus has specific sources of error (*e.g.* constance of the balance over 24 h) and varying the relative humidity no longer has a systematic affect on the results.

The reproducibility of the traditional Enslin-Neff method is strongly influenced by variations in ambient conditions in the laboratory (particularly temperature and relative humidity). Application of the Dieng method in different laboratories with varying ambient conditions will lead to improved reproducibility and comparability of results. In addition, results from the Dieng apparatus can be collected using a connected computer and this represents an important advance also.

**Key Words**—Bentonite, Dieng Apparatus, Enslin Method, Enslin Neff, Water-uptake Capacity.

### INTRODUCTION

A method for determining the water-uptake capacity of powders was proposed by Enslin (1933). He claimed that the method could be applied to viscose silk, specific celluloses, soap, paint, glue, gelatine, adhesives based on starch, biological samples, and soils. He also claimed that wettability (hydrophilicity) *e.g.* for the optimization of ore processing by flotation, can be determined. For the measurement, a pulverized sample is placed on a frit by pouring a weighed amount through a funnel. The frit is in contact with excess water and the flask containing the water is connected to a horizontally arranged burette (Figure 1). The amount of water which is taken up by the powder can be read from the burette. In order to prevent evaporation (which could appear to increase water-uptake capacity) the flask is sealed using a lid. However, accurate reproducibility of results using this method has been difficult. Based on a critical evaluation of possible interfering parameters, Neff (1959) proposed a modified device which was reviewed by Köhler and Herzog (1965) who in turn proposed elimination of the effect of different sample weight by adding 0.5% isobutylalcohol which increases the wettability of the water.

The ‘Enslin-Neff’ apparatus became famous in Germany, and in some neighboring countries, and almost all publications regarding the reproducibility and physical meaning of the Enslin-Neff values are in German. In Germany today the Enslin-Neff method is used in clay mineralogy (*e.g.* bentonite quality control), soil science (*e.g.* soil classification), material science, and pharmacy. It is included in the German industry norm (DIN 18132) being relevant for civil engineering (*e.g.* evaluation of building ground and construction of landfills). The Enslin-Neff method, regardless of the exact variation and resulting accuracy, is surprisingly successful, particularly in the bentonite industry and civil engineering. The Enslin-Neff values are known to be determined by the amount of exchangeable Na<sup>+</sup> and to a lesser extent by the smectite content (Neff, 1959). The Na<sup>+</sup> content in turn is known to significantly affect swelling characteristics and rheological parameters such as plasticity. Hence the Enslin-Neff method provides an indirect estimate of the Na<sup>+</sup> content and the option to avoid laborious determination of the amount of exchangeable Na<sup>+</sup>, *e.g.* by inductively coupled plasma-mass spectrometry after CEC experiments. However, for detailed investigation of a water-uptake mechanism (*e.g.* influence of the mesopore system determined by the micro fabric), a set of bentonites, each with different properties, has to be considered.

The relatively poor reproducibility of results (3–4% standard deviation) using the Enslin-Neff apparatus continues to be a major consideration. According to

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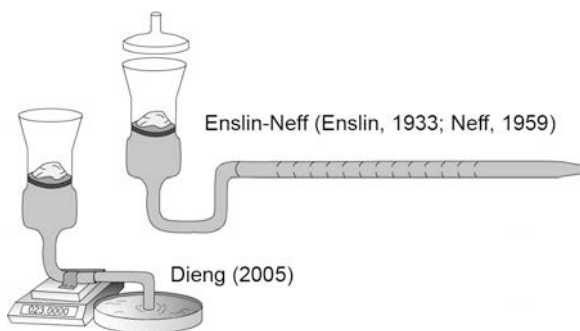


Figure 1. Sketch of the established Enslin-Neff device and of the new device proposed by Dieng (2005).

Böhler (1993), the main problem is evaporation, a point acknowledged by Enslin himself (1933). Correction of the evaporation, based on parallel measurements, without sample, was suggested by Demberg (1991) and Kugler *et al.* (2002). However, this does not lead to correct values since the air-water interface is different between a wetted sample covering a substantial area of the frit and the frit only (Böhler, 1993). Evaporation was ~10% less if a sample was placed on the frit (Kugler *et al.*, 2002).

In order to eliminate all evaporation effects, the Enslin-Neff device was further modified (Dieng, 2005, 2006), so that water uptake is measured gravimetrically. Interestingly, a weight-based water-uptake device had previously been constructed (Köhler and Herzog, 1965) in order to compare the Enslin with the Enslin-Neff apparatus. Although it was claimed that this device worked well, it was not developed further. A proposal to measure the weight loss of the water reservoir was made by van der Kamp *et al.* (1986). However, because it is an open system, this reservoir (cup of water) is also in danger of losing weight by evaporation. In contrast, Dieng (2005, 2006) proposed direct weighing of the water uptake. The principles of the traditional Enslin-Neff method and the new modification of Dieng are shown in Figure 1.

The old and the new apparatus are compared in this study, with respect to reproducibility of results and the influence of ambient conditions.

## MATERIALS AND METHODS

In this study, two different bentonite samples with a comparably large amount of exchangeable  $\text{Na}^+$  (IB 8) and  $\text{Ca}^{2+}/\text{Mg}^{2+}$  (IB 13), respectively, were selected. The bentonites, which are part of a sample set described in detail by Kaufhold and Dohrmann (2008), Kaufhold *et al.* (2008), and Ufer *et al.* (2008), were dried at 60°C until the weight was constant, and then ground to <250  $\mu\text{m}$  using a hammer mill. The chemical composition was investigated by X-ray fluorescence (XRF – Phillips PW 1480). The mineralogical composition was

determined by X-ray diffraction (XRD) analysis, using a Phillips PW 3710 device with  $\text{CuK}\alpha$  radiation, and quantified using the Rietveld software AutoQuan<sup>®</sup> (Bergmann and Kleeberg, 1998). The smectite structure model was provided by Ufer *et al.* (2004). The cation exchange capacity (CEC) was measured using the Cu-triethylenetetramine method (Meier and Kahr, 1999). The CEC value was determined by inductively coupled plasma-atomic emission spectroscopy and used for the correction of the erroneous  $\text{Ca}^{2+}$  value according to Dohrmann (2006). Results are presented in Table 1.

The water-uptake capacity of both bentonites was determined according to Neff (1959) using two different burettes as well as the recently modified device (Dieng, 2005, 2006). The sample weights were 0.3 g and 0.5 g, respectively. The samples were placed on the frit using the recommended funnel method. For each experimental variation, five replicates were recorded, to check reproducibility. The results of all replicates were recorded after 24 h as specified by the method described in DIN 18132. Furthermore, DIN 18132 suggests that the effect of evaporation from the burette be eliminated by subtracting the evaporation determined from a separate burette filled only with water. As mentioned above, this leads to underestimation of the water-adsorption results by ~10%. In addition, the evaporation differs from one burette to another. Therefore, in this study the evaporation rate of each burette was determined prior to the experiment, according to Kugler *et al.* (2002) and the evaporated water (after time  $t$ ) subtracted from the final result. Hereafter, this correction is referred to as the ‘improved evaporation correction’. However, using this procedure, evaporation will still be overestimated because of the different solid-gas interface with and without sample on the frit, leading to underestimation of the water-sorption value.

Additionally, the effect of gently compressing the sample mount was studied by two replicates for each bentonite (standard = funnel method; compressing = changing the form of the sample mound by gentle pressing). The results are commonly given as ‘Enslin Neff values’ in g/g. In this study, the values were converted to wt.% water uptake compared to sample weight, in order to be able to directly compare the effect of different sample weights. All values are given with and without improved evaporation correction.

In order to systematically investigate the effect of ambient conditions on the water-uptake capacity, additional tests were performed under well defined conditions (in a climate oven).

## RESULTS AND DISCUSSION

The results obtained under laboratory conditions are listed in Table 2 and statistical interpretation of the data presented in Table 2 is given in Table 3. The data presented in Tables 2 and 3 are interpreted either by

Table 1. Basic characterization of the two bentonite samples used in this study.

Location	B8 Wyoming	B13 Hungary
Mineralogical composition	Na-montmorillonite (~64%) Quartz (23%) Feldspar (8%) Muscovite (2%) Heulandite (2%) Calcite (1%)	Ca/Mg-montmorillonite (~86%) Quartz (6%) Calcite (3%) Kaolinite (2%) Anatase (2%) Feldspar (1%)
Cation exchange capacity		
Na <sup>+</sup> (meq/100 g)	69	1
Na% (%)	99	1
K <sup>+</sup> (meq/100 g)	0	2
Mg <sup>2+</sup> (meq/100 g)	1	38
Ca <sup>2+</sup> (meq/100 g)	16	75
Ca <sup>2+</sup> corrected by T-value (meq/100 g)	1	46
Ca% (%)	23	89
S value <sup>†</sup> (meq/100 g)	86	116
CEC (meq/100 g)	71	87
S-T <sup>‡</sup> (meq/100 g)	15	29
Chemical composition (wt.%, main elements)		
SiO <sub>2</sub>	66.8	44.6
TiO <sub>2</sub>	0.1	2.0
Al <sub>2</sub> O <sub>3</sub>	15.7	16.2
Fe <sub>2</sub> O <sub>3</sub>	3.1	10.1
MnO	0.0	0.1
MgO	1.5	2.1
CaO	0.9	3.1
Na <sub>2</sub> O	2.6	0.1
K <sub>2</sub> O	0.4	0.6
P <sub>2</sub> O <sub>5</sub>	0.0	0.3
(SO <sub>3</sub> )	0.2	0.0
LOI	8.3	20.4
Sum	99.7	99.6

<sup>†</sup> Sum of cations

<sup>‡</sup> CEC, determined using the index cation.

considering the absolute mean values ('mean value' in wt.%) or by considering the standard deviation as a percentage of the water-uptake capacity. The standard deviation determined for burettes 1 and 2 accounts for 2.6% and 4.5%, respectively. The resulting mean value of 3.5% was used as the error bar in Figures 2 and 3. Approximately the same standard deviation was found for the Dieng method (3.3% on average).

The reproducibility of the Enslin-Neff method can be improved significantly (<2% standard deviation) if the values are corrected for evaporation rates specific to each burette (Kugler *et al.*, 2002) and this was confirmed in the present study. By considering the evaporation (improved evaporation correction), a mean standard deviation of all measurements performed by the old method of 1.9% was found. However, as discussed above, the area of the frit available for evaporation (area of the frit being in contact with air which takes up water by evaporation) is reduced after addition of the sample

because the area covered by the sample is no longer available for evaporation after addition of the sample. Therefore, even these values clearly suffer from systematic errors.

The Dieng method, in contrast, is claimed to operate correctly regardless of evaporation effects. Nevertheless, a reproducibility of <2%, which was expected based on the above-mentioned results, was not attained in this study.

The water-uptake capacities of both bentonites are presented (Figure 2) for each of two different sample weights, both with and without evaporation correction. The Dieng values are slightly greater than those obtained by evaporation correction, which probably reflects the exaggerated evaporation correction (smaller evaporation rate for frit with sample than for the frit without a sample, as explained above).

In addition, no systematic effect of the burette could be identified. That different burettes perform differently

Table 2. Results of all measurements of water adsorption capacity (values in bold show significant deviation).

Apparatus		Sample weight (g)	B8 Uncorrected (wt.%)	B13 Uncorrected (wt.%)	B8 Corrected (wt.%)	B13 Corrected (wt.%)
Burette 1	funnel	0.3	510	200	506	<b>191</b>
Burette 1	funnel	0.3	519	189	491	154
Burette 1	funnel	0.3	540	181	509	153
Burette 1	funnel	0.3	535	193	505	154
Burette 1	funnel	0.3	545	188	514	152
Burette 2	funnel	0.3	491	<b>276</b>	489	156
Burette 2	funnel	0.3	480	196	472	144
Burette 2	funnel	0.3	471	171	469	<b>171</b>
Burette 2	funnel	0.3	529	165	477	<b>126</b>
Burette 2	funnel	0.3	521	171	502	143
Dieng (2005)	funnel	0.3	485	162		
Dieng (2005)	funnel	0.3	504	161		
Dieng (2005)	funnel	0.3	542	158		
Dieng (2005)	funnel	0.3	528	167		
Dieng (2005)	funnel	0.3	493	162		
Burette 1	funnel	0.5	487	177	464	153
Burette 1	funnel	0.5	478	180	458	153
Burette 1	funnel	0.5	452	174	446	154
Burette 1	funnel	0.5	468	177	457	155
Burette 1	funnel	0.5	477	177	464	156
Burette 2	funnel	0.5	470	170	453	148
Burette 2	funnel	0.5	478	171	467	150
Burette 2	funnel	0.5	466	165	459	150
Burette 2	funnel	0.5	475	181	463	149
Burette 2	funnel	0.5	477	<b>214</b>	467	<b>162</b>
Dieng (2005)	funnel	0.5	487	167		
Dieng (2005)	funnel	0.5	488	155		
Dieng (2005)	funnel	0.5	487	166		
Dieng (2005)	funnel	0.5	462	155		
Dieng (2005)	funnel	0.5	503	163		
Dieng (2005)	Compressed	0.3	594	119		
Dieng (2005)	Compressed	0.3	594	128		

is known from laboratory practice, but this could not be proved statistically in this study.

One additional source of error might be the form of the sample heap. In order to minimize this effect,

Table 3. Statistical interpretation of the data presented in Table 2 (uncorrected values).

Apparatus	Replicates	Outliers not considered	Sample	Sample weight (g)	Mean value (wt.%)	Mean deviation (wt.%)	Standard deviation (%(wt.%)	
Burette 1	5		funnel	IB8	0.3	530	12	3
Burette 2	5		funnel	IB8	0.3	498	21	5
Dieng (2005)	5		funnel	IB8	0.3	510	20	5
Burette 1	5		funnel	IB8	0.5	472	10	3
Burette 2	5		funnel	IB8	0.5	473	4	1
Dieng (2005)	5		funnel	IB8	0.5	485	9	3
Burette 1	5		funnel	IB13	0.3	190	5	4
Burette 2	5	1	funnel	IB13	0.3	176	10	8
Dieng (2005)	5		funnel	IB13	0.3	162	2	2
Burette 1	5		funnel	IB13	0.5	177	1	1
Burette 2	5	1	funnel	IB13	0.5	172	5	4
Dieng (2005)	5		funnel	IB13	0.5	161	5	4
Dieng (2005)	2		compressed	IB13	0.3	124		
Dieng (2005)	2		compressed	IB8	0.3	594		

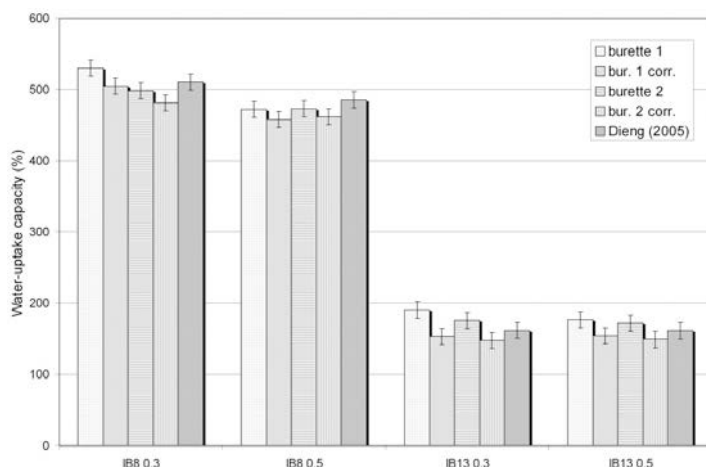


Figure 2. Water-uptake capacities of bentonites IB8 and IB13 (two weights) using two different burettes, with ('corr.') and without improved evaporation correction, and results obtained by the Dieng (2005) method. All results are mean values derived from five replicates.

DIN 18132 recommends passing the powder through a funnel. In the present study no systematic effect of slight variations of the sample heap form could be found. On the other hand, compressing the sample heap on the frit to a flat disc did affect the result (Figure 3). For the two replicates studied, the water-uptake capacity of the Na-bentonite increased while the value for the Ca-bentonite decreased slightly. This indicates the interplay of different mechanisms. Generally, the water-uptake capacity of bentonites is known to occur as a result of crystalline swelling (interlayer expansion) as well as the capillary system (pore system of powder). The capillary system is believed to be affected by compressing. The water-uptake capacity of pellets which were produced by compaction of the sample powder was investigated by Kugler *et al.* (2002) who found that the values obtained by measuring the Enslin-Neff water-uptake capacity of the pressed pellets were in good agreement with the water-uptake capacity of powder determined at 75% relative humidity, the latter being more or less independent of the capillary system, as adsorption occurs by the gas phase only. It can probably be concluded that the capillary pore system was reduced by compaction in

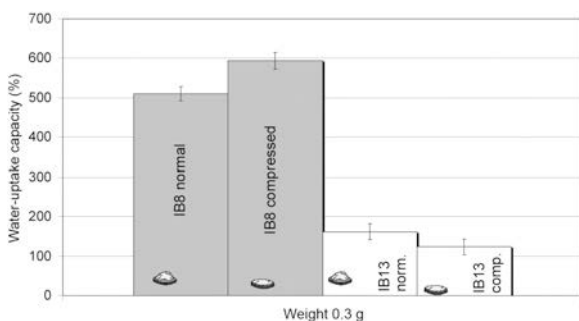


Figure 3. Effect on the results of differences in the form of the sample heap.

such a way that water uptake was governed by crystalline swelling only.

The results obtained in this study may indicate that compressing the sample heap affects the capillary systems of Ca/Mg- and Na-bentonites in different ways. In order to prove this, further research regarding the microstructure of Ca/Mg-bentonites compared to Na-bentonites is required.

With respect to the reproducibility of results from the Enslin method, slight differences in the form of the sample heap thought unlikely to have affected the results significantly. Therefore, the influence of ambient conditions (especially temperature and relative humidity) is believed to be the main source of error. In this respect, the Dieng method should be better since evaporation and/or water adsorption from air does not affect the result. In order to investigate this point systematically, both bentonites were measured using the Dieng method under constant ambient conditions. For this, the whole apparatus was placed in a climate oven under different relative humidities (30, 60, 90%) at 30°C.

Using the Dieng apparatus, no systematic effect of ambient conditions on the water-uptake capacity was observed (Figure 4). In case of Na-bentonite, the values recorded at 24 h vary from 537 to 553 wt.%. The same range of deviation (16 wt.%) was found for the Ca-bentonite. This range (~15 wt.%, corresponding to ~5 g of water-uptake capacity) actually represents the accuracy of the device as applied. The conditions in the oven (ventilated in order to ensure homogeneous humidity and 30°C which is required for humidity constance) probably affect the reproducibility of these experiments, in particular in relation to the balance itself. Nevertheless, observations here proved that evaporation and/or water adsorption caused by varying ambient conditions does not affect the values measured by the Dieng (2005, 2006) device.

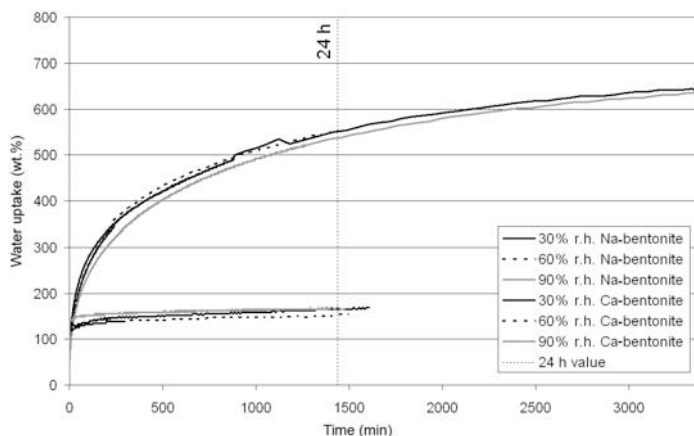


Figure 4. Water-uptake capacity of both bentonites measured using the Dieng apparatus at relative humidity ranging from 30 to 90%.

## CONCLUSIONS

Evaporation is known to have a serious affect on the water-uptake capacity values measured by the Enslin-Neff device. Performing 'improved-evaporation corrections' by considering water loss without a sample (as suggested by Kugler *et al.*, 2002) was found to improve reproducibility. However, the evaporation rate of the burette with and without a sample on the frit is known to differ. Hence, even this evaporation correction leaves some uncertainty. This study has shown that ambient conditions (relative humidity 30–90%) did not affect the results when using the Dieng apparatus and that the results obtained by the Dieng method in fact lie between the uncorrected and corrected Enslin-Neff values.

In addition, results confirmed that the improved evaporation correction of results from the old apparatus improves reproducibility to <2% as stated by Kugler *et al.* (2002). Therefore, a reasonable degree of reproducibility of the results from the Dieng apparatus was expected. However, a reproducibility of <2% was not attained, and this is not caused by evaporation. Hence, the Dieng apparatus introduces different sources of error, *e.g.* the accuracy of the balance, which needs to be constant over the 24 h period in question. Other possible sources of error will be investigated in future work.

The reproducibility of results from the traditional Enslin-Neff method is very much influenced by the variation of ambient conditions in the laboratory (temperature and relative humidity) which particularly affects the comparability of results obtained by different laboratories. Accordingly, the application of the Dieng method in a laboratory with varying ambient conditions is expected to lead to improved reproducibility of results and reliability of cross-laboratory comparisons (with different ambient conditions). The Dieng apparatus may also be connected to a computer for digital recording of results, which would represent an important advancement.

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