**IAB – Institut für Angewandte Bauforschung
Weimar gemeinnützige GmbH**

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Flüssigböden e.V

Über der Nonnenwiese 1 • 99428 Weimar
+49 3643 8684-0 +49 3643 8684-113
kontakt@iab-weimar.de www.iab-weimar.de

INVESTIGATION REPORT IAB 2039

Short title:	STABINO
Order case:	Zeta potential and charge titration to assess the stability of suspensions to offer IAB-BS 20/19 of 15.04.2019
Client:	Colloid Metrix GmbH Herr Kai Gossmann Am Latumer See 11-13 40668 Meerbusch
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Dr.-Ing. Ulrich Palzer Institutsdirektor	Dr.-Ing. Barbara Leydolph Leiterin des Forschungsbereiches

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1 Reason for investment

With the investment in a zeta potential measuring device, the IAB - Institut für Angewandte Bauforschung Weimar gGmbH (IAB*)* - is intended to increase performance in the following areas:

Binders: The aim is to optimise the formulation stability of calcined clays using suitable construction chemical additives. The effect of electrostatic repulsion on the product properties of calcined clays is to be determined.

Mortar and concrete: Investigation of the effect of construction chemical admixtures (additives) on the rheological behaviour of cement-based or alkali activated binding agents for use in mortar and concrete. The aim is to determine suitable additives, such as polycarboxylate ethers (PCE), and their effects on the electrostatic and steric repulsion.

Ceramic raw materials and materials: Evaluation of the charge conditions of particle surfaces in ceramic slurries for the stability ranges of a dispersion, aggregation or flocculation as well as of suspensions of thermally activated clay raw materials. An additional application is the optimization of the surface modification of "layered silicate-geo-polymer nanocomposites" for the production of coatings.

2 Institute profile

The Research Institute IAB - Institut für Angewandte Bauforschung Weimar gGmbH - sees itself as a partner and mediator between university basic research and practice-relevant problems in wide areas of the building industry. The scientific competence at the IAB covers the subject areas of building materials and process engineering, building systems and components, civil engineering and pipeline construction up to energy and building services engineering.

In the research field of building materials, research and development tasks in the field of raw material extraction, production, processing and product development are carried out in close cooperation with companies in the building materials industry. The focus is on material optimizations that make products and processes more energy efficient, sustainable and safe.

Extensive material, chemical, mineralogical and ceramic technological investigations are carried out to ensure the performance of high-quality starting materials and end products, not only for the ceramic industry.

3 Selection of the measuring system

3.1 Measurement methods - state of the art

In general, a distinction is made between the three measuring methods listed below, which are used to determine the zeta potential. Table 1 provides a comparison of the scope of measurement.

Electroacoustics
The electroacoustic method uses the interaction of the particles and their charge envelopes with ultrasonic waves to calculate the zeta potential. To do this, the suspension is first excited by ultrasound. The charge cloud that is set in oscillation emits an electric vibration potential wave. This signal is then converted into the zeta potential.

Electrophoresis
The particles in a suspension move in the electric field *E* by electrostatic attraction with the velocity *v* in the direction of the oppositely charged electrode. The electrophoretic mobility *μe* in the electric field *E* can be calculated from these two measured parameters. From this, the zeta potential is determined [1].

Streaming Potential
The streaming potential measuring principle is based on the fact that the loosely bound cations in the bilayer at the interface of two immiscible phases [2] are moved by mechanical forces (streaming). In this case the flow is caused by a plunger movement. The greater the amount of charges suspended at the shear plane (interface between firmly and loosely bound cations), the higher the amount of cargo shifted. By means of two electrodes along the flow, the electrical voltage difference - the current potential - is measured. The zeta potential can be derived from the current potential according to the Helmholtz - Smoluchowski - formula. [3].

Table 1: Measuring scope of the different zeta potential measuring methods

	Electroacoustics	Electrophoresis	Streaming potential
Particle size range	5 nm - 100 µm	0,3 nm - 10 µm	0.3 nm - 300 µm
Sample concen-tration	0,1 - 50 Vol.-%	0.1 ppm - 40 Vol.-%	0.001 - 40 Vol.-%
Sample volume	0.5 ml	20 µl	from 950 µl to 10 ml

3.2 Decision criteria - selection of the measuring method

The streaming potential principle covers a wide range of particle sizes and concentrations and is therefore perfectly suited for the above mentioned research purposes at the IAB. A further advantage of this measuring method is that no additional sample parameters, such as pure density or dielectric constant, of the starting materials for measurement of the zeta potential are required.

The demonstration of the streaming potential measuring device STABINO from Colloid Metrix was fully convincing. Due to the characteristics mentioned in table 1 and the positive feedback during the demonstration, the decision was made in favour of this device. As an additional service, a 2-day detailed training on theoretical basics and measurement on the device was carried out.

Figure 1: Workplace at IAB Weimar

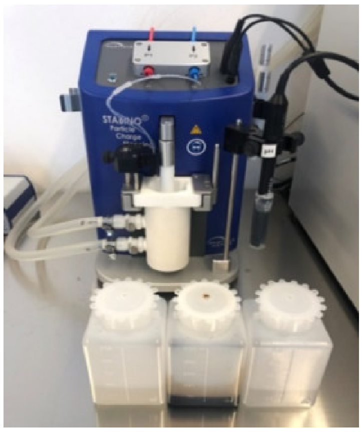

Figure 2: Detailed view - STABINO

Selection criteria for the measuring instrument STABINO:

- Handy, space-saving and low-maintenance desktop unit,
- Especially suitable for R&D projects:
  - optimal sample quantities lead to meaningful results,
  - various titration volumes and measuring intervals adjustable,
  - wide measurable particle size range due to four differently designed volumetric flasks,
  - two titration units for switching between different additives.
- Acquisition of additional material parameters (conductivity, temperature, pH value),
- Easy cleaning of the measuring cell with deionized water or acetone.

4 Application Examples

4.1 Application example 1: Alternative binders

Research objective: Evaluation of mineral surfaces (particles)

By evaluating the surface charges of calcined clay mineral containing powders by PolyDADMAC titration, suitable additives shall be determined. In this context the influence of the chemical-mineralogical composition of the starting material, the firing temperature and firing atmosphere on the zeta potential will be investigated.

Figure 3: Sample material from calcined clays before preparation to powder

The following figure 4 shows the course of the zeta potential of slurried kaolin and metakaolin produced from it. This test series was carried out on suspensions with a solids content of 5 Ma.% in demineralized water.

As a result, a significant dependence of the surface charge on the firing temperature can be determined. For example, kaolin or metakaolin (MK) tempered at 700 °C has a starting potential of -50 mV, which drops to -75 mV at MK 900 °C. This means that for a higher-fired metakaolin, fewer additives for long-term stabilization would have to be used than for a low-firing metakaolin.

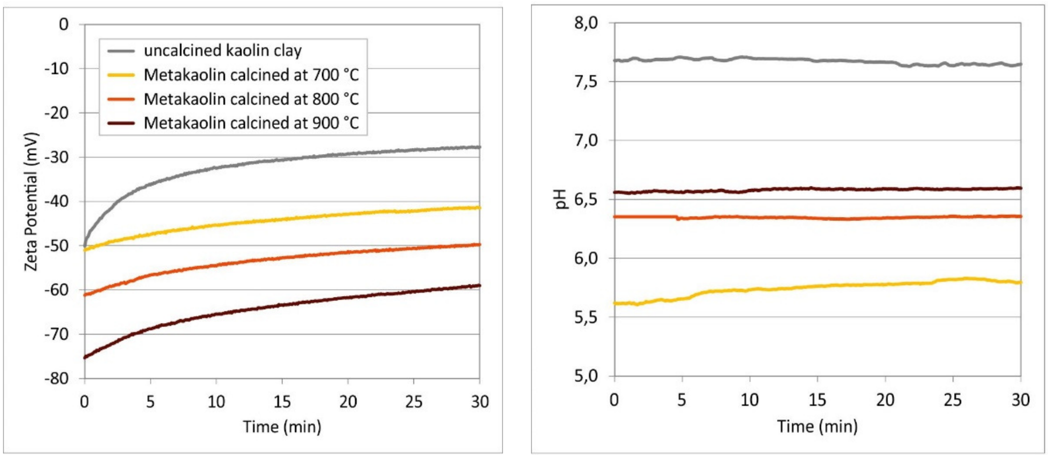

Figure 4: Zeta potential and pH value of slurried or tempered kaolin

Furthermore, a destabilization or agglomeration of the particles in these suspensions can be observed as a function of time, which is induced by the natural aging process. This finding has the potential to define a further optimization parameter for the production of metakaolin for use as an alternative binder system. The overall goal is the production of surface-doped MetaTones.

4.2 Application example 2: Mortar and concrete

Research objective: Optimisation of mineral material systems [4].

The aim is to gain knowledge about the formation of surface charges of alternative binder particles in the alkaline medium to ensure a homogeneous distribution of the particles in the mineral material system. The overall objective is to investigate the effect of construction chemical additives on the rheological behaviour of cement-based or alkali activated binder glues (geopolymer) in mortar and concrete. Additives which induce electrostatic and steric stabilization and impoverishment stabilization are included in the investigations. The following SEM Fig. 5 shows a hardened mineral material system in which cracking has occurred as a result of insufficient dispersion of the binder component metakaolin.

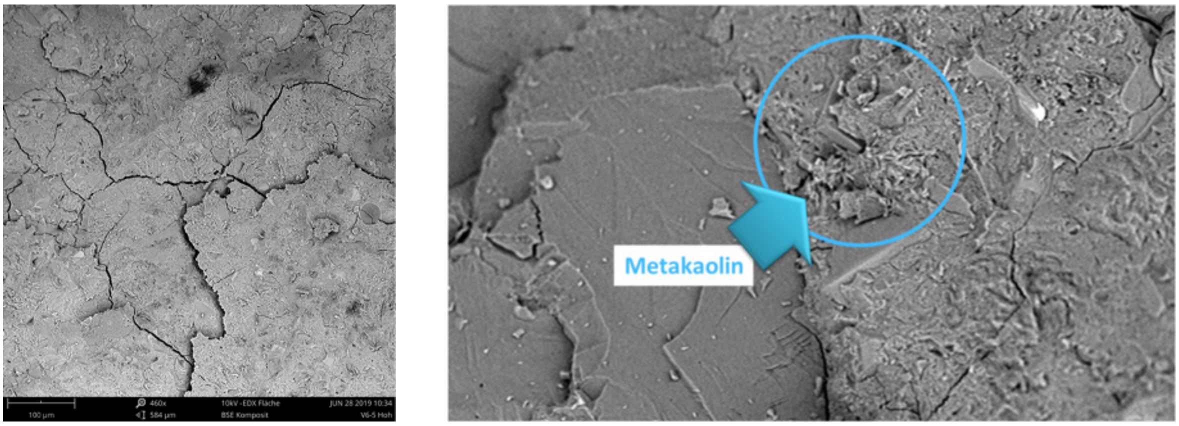

Figure 5: REM Image IAB Weimar at the fracture surface of a geopolymer (right magnified)

In order to investigate the effect of additives on mineral material systems, several series of measurements were first carried out with metakaolin, which are shown below as examples. The aim of the test series was to investigate the influence of different additives (e.g. concrete admixtures) on the zeta potential of metakaolin in water-based suspensions.

Mineral substance system Metakaolin
The metakaolin under investigation, ARGICAL M1000, is a calcined kaolin, which is a natural, tempered pozzolan according to DIN EN 197. As produced, pozzolan is used as a binder component of Portland cement or in mineral geopolymers in the production of mortar and concrete. The material characteristics of the calcined sample are shown in Table 2.

Table 2: Substance characteristics of metakaolin ARGICAL M1000

Chemical composition	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**K_2O+Na_2O**	**CaO+MgO**
	55 %	40 %	1.4 %	1.5 %	.,8 %	0.3 %
Particle size distribution	80 µm < 95 %					
Specific surface area BET	17 m^2/g					

Sample Preparation
The starting materials must have a uniform grain size or be processed accordingly. This is necessary in addition to the generation of a representative sample, since the maximum possible particle size is limited by the mechanical design of the measuring cell and displacer piston. For particle sizes ≤100 µm the use of a "400 µm displacement piston" is recommended.

Measurement 1
The Teflon measuring cup used has a capacity of 10 ml. For the experiments with Metakaolin M1000 the concentration ranges 5, 10 and 15 wt.% were selected and suspensions with deionized water were prepared.

For all measurements a constant temperature of 22 °C was set by means of a thermostat. Initially, status measurements of the suspensions without additives were performed and start potentials of -15 to 20 mV for metakaolin were measured. Then the actual titrations were performed.

The titrations shown in Figure 6 were carried out with a diluted potassium silicate solution (WGM = 1.0). At least one double determination was carried out for each concentration range and each additive to check the reproducibility of the results. As the pH and conductivity are determined automatically, these parameters are also shown as a diagram.

The optimal titration regime for the metakaolin M1000 was 32 sec and 25 µl. A measurement with the total titration volume of 1 ml therefore took about 20 min.

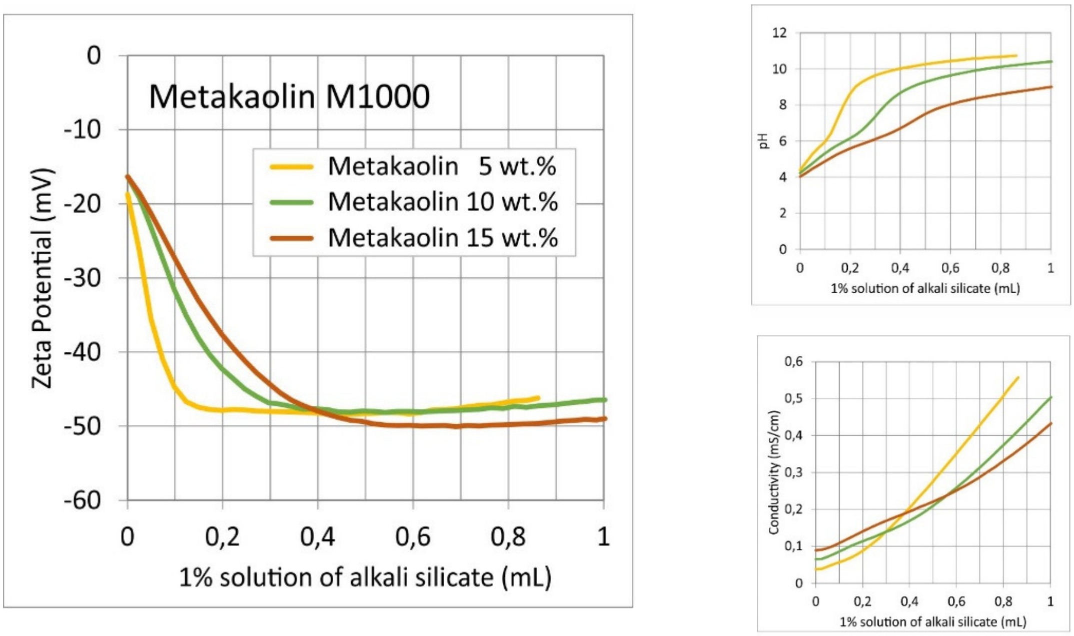

Figure 6: Zeta potential of metakaolin M1000 in dilute potassium silicate solution (titration)

Measurement 2

The following Figure 7 shows the development of the zeta potential for metakaolin M1000 with a proportion of 5 wt.% in the suspension as a function of the amount of additive added.

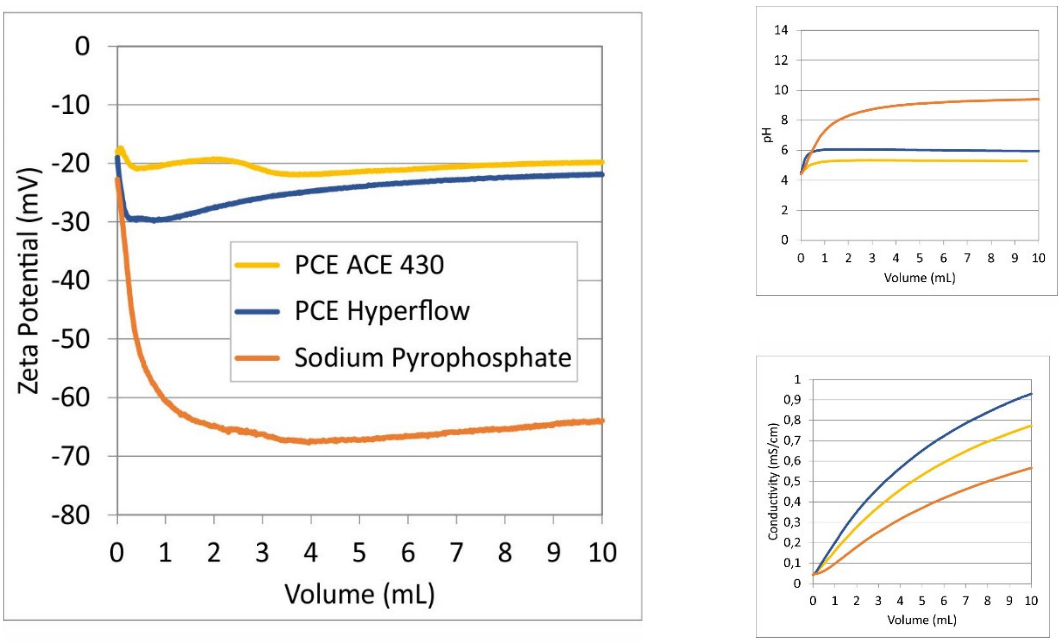

Figure 7: Titration with various additives (20 Ma.-% / 22°C)

Evaluation

The aim of the listed series of measurements was to stabilize the metakaolin-water suspension by titration of various additives. If the stabilization is carried out by means of electrostatic repulsion, the highest possible zeta potential (positive or negative) should be achieved.

If, on the other hand, titration is carried out to the isoelectric point (zero point), coagulation of the particles occurs and thus flocculation within the suspension. As can be seen in Figure 6, an average of 0.6 ml of the 1% potassium water glass was used to increase the zeta potential by 35 mV (from -15 to -50 mV). This corresponds to an optimum addition of 6 g undiluted potassium silicate solution K57M per kg metakaolin M1000.
With sodium pyrophosphate the highest stabilization around 50 mV was achieved. The Concrete admixtures (PCE), on the other hand, have no serious influence on the zeta potential of metakaolin, but have a stabilizing effect on suspensions due to their steric repulsion.

Table 3 shows an overview of all required quantities of the various additives (titration solutions).

Table 3: Calculation of the amount of undiluted additive

Additives	Additive per 100 g metakaolin	Max. zeta potential
Alkalisilicat K57M	0,4 - 0,8 g	-50 mV
Natriumpyrophosphat	350 - 470 g	-65 mV
PCE (ACE 430)	12 - 24 g	-21 mV
PCE (HyperFlow)	20 - 40 g	-30 mV

Processing and material properties can be improved by determining suitable additives and adding them in optimum quantities.

4.3 Application example 3: Ceramic raw and other materials

Research objective: Optimization of processing properties

Field of activity 1: Production of building ceramics products
For the production of building ceramic products, additives are used to influence the processing properties. By adding surface-active substances to these mineral material systems, the surface charge of the clay minerals or their accompanying minerals contained therein and thus the processing properties (e.g. plasticity) are influenced.

Field of activity 2: Layered Silicate-Polymer Nanocomposites
Another application is the optimization of the surface modification of "layered silicate-polymer nanocomposites" for the production of mineral coating systems.

Field of activity 3: Investigations of flocculants as separation processes
Many building materials require sand and gravel, and their treatment produces between 3-15% gravel washing sludge. This fine grain fraction suspended in water consists mainly of clay minerals. To make the fine grain fraction available, suitable flocculants are used.

5 Conclusion

The Zeta Potential Analyzer STABINO manufactured by Colloid Metrix GmbH is a target-oriented extension of the existing analytical instrument infrastructure at the IAB. For the described research objectives and existing analysis methods, the application of the measuring device was able to verify already gained knowledge and to expand the research horizon in many ways. Provided that the sample is carefully prepared with regard to the weight and homogeneity of the sample, measurements with this instrument lead to reproducible results.

In addition to its user-friendliness, the table-top unit also convinces with its comparatively low purchase costs. It is almost maintenance-free and the measuring instruments are easy to clean. The customer service is also convincing due to competent employees, who take care of any questions and problems, be they hardware or software related or even theoretical. Together with the user, uncomplicated solution proposals are developed and promptly implemented.

List of figures

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Bibliography and sources

[1] Colloid Metrix GmbH: www.particle-metrix.de. [Online] [Zitat vom: 29. 01 2020.] https://www.particle-metrix.de/technologien/nanopartikel-tracking/artikel-nanopartikel-tracking/zetapotential-bestimmung-mit-hilfe-der-elektrophorese-methode.

[2] Schultze, Wolfgang: Dispersions-Silikatsysteme. 71272 Renningen-Malmsheim : expert Verlag, 1995. ISBN 3-8169-1222-2.

[3] Colloid Metrix GmbH: www.colloid-metrix.de. [Online] [Zitat vom: 22. Januar 2020.] https://www.colloid-metrix.de/fileadmin/pdf_applications/C10_Stabino_Stroemungspotential_DE.pdf.

[4] Ruy A. S´a Ribeiro, Marilene G. S´a Ribeiro, Gregory P. Kutyla, Waltraud M. Kriven: Amazonian Metakaolin Reactivity for Geopolymer Synthesis. In: Advances in Materials Science and Engineering. Volume 2019 Article ID 8950764, (2019).