A FAST TESTING METHOD TO CHARACTERIZE ASHES AND ASH MIXTURES USING THE ULTRASONIC TECHNIQUE

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ABSTRACT

Fly ash is a typical mortar constituent in Germany, other European countries and worldwide. If cement alone is used as a binder, then the mortar is too expensive and cannot provide all properties. That`s why many companies have special recipes with fly ash, especially hard coal fly ash components, in the mortar. The aim of this project is to substitute such fly ashes by lignite coal fly ashes, which are cheaper, available at every times or have better properties. However this means, that the calcium free or calcium poor ash should be substituted by calcium rich ashes, which are not certificated because of fluctuations.

To compensate the fluctuations in the ash compositions, several ashes are mixed. The European standard EN 450, which contains requirements, for example for the chemical composition of ashes, has to be taken into account. Fly ash mortar compound prisms have been produced and the different mechanical and deformation values were determined in comparison to a reference material.

The basis for all experiments was the recipe of the company for a special mortar. An ash compound could be developed with the same workability by considering the economic reasons of the company. An important result too is that the fluctuations of the fly ash batches can be controlled by special developed chemical (color test) and physical (Ultrasonic velocity) test methods.

Keywords: fly ash, mortar components, ash compound, ash fluctuations, chemical composition, chemical and physical test methods

INTRODUCTION

The use of fly ash components in mortar and, of course, concrete recipes is state of the art worldwide. Cement reduction, improvement of the workability, increase of the durability and creation of strength reserves are some aspects for doing this. In Germany in the 90s of the last century many investigations were performed in this direction (1). The most common materials are hard coal fly ashes (F-ashes) with a high puzzolanic reactivity and with a little lime (CaO) content (2,3). Economical and technological problems in power plants can lead to delivery difficulties. That's why companies in Germany are looking for other materials on the basis of ashes, which have the same or better properties. Such materials can be lignite coal fly ashes (C-ashes), which are available all the time (4,5,6). With this decision of the companies many problems are connected: such fly ashes are not certificated, they have a content of calcium oxide or other constituents which are too high and often show great fluctuations in their compositions. On the other hand, such fly ashes have a great potential as a component of mortar recipes because of their self-hardening properties, not only in cementitious systems (7,8). If it were possible to combine two or more fly ashes purposefully to control the calcium oxide content and, at the same time, to eliminate the fluctuations, many application areas would be opened up. The following paper shows solution paths for using fly ash compounds in a special mortar recipe.

RESEARCH SIGNIFICANCE

Fly ashes are state of the art worldwide in using ashes in mortars and concretes. Lignite coal fly ashes can be used only in special fields of mortar technologies, but have a great potential because of their reactivity behavior. A wider use is prevented by two facts: their chemical compositions, which do not correspond to the standards and their fluctuations between different batches. Most of the studies on these admixtures were carried out with special batches of power plants and the results cannot always be transferred to other batches or ashes of the same or other plants. The authors believe that this detail study, dealing with the creation of mixture rules of different ashes and with the development of test methods to control the fluctuations, can be very useful to mortar and of course concrete technology.

EXPERIMENTAL INVESTIGATION

The investigations were carried out with three ashes from different power plants. Additionally two batches of each ash were chosen to determine the fluctuations in the chemical and mineralogical composition. That's why the first step of our investigation procedure was to characterize the starting ash materials. Based especially on chemical compositions certain mixture ratios between different ashes could be calculated. Using the starting materials and the calculated mixtures, the second step was the production of mortar bars to determine a lot of mortar properties (reactivity, workability, shrinkage, swelling, strength, dynamic modulus of elasticity). The basis for the investigations in the Lab was a common mortar recipe according to the cement test procedure. For the investigations in the Field a special recipe was used, given by our research partner. The important third step included the development of an accelerated test procedure for the determination of mixtures, because the mortar producer must be able to react quickly to fluctuations. A color test and an ultrasonic measurement system were also tested.

Materials

Three fly ashes from different power plants and two batches from each ash were investigated. The chemical and mineralogical compositions are summarized in **Table 1**. Fly ash 1 is a silicium and aluminium rich material with a very less amount of calcium oxide. There are no significant fluctuations between the two batches measured. Fly ash 2 is also silicium and aluminium rich, but with a lower amount of silicium in comparison to fly ash 1. The whole calcium oxide content is a little bit higher than in fly ash 1. Differences between the two batches of ash 2 exist in the mullite content, in the amorphous amount and their composition. Fly ash 6 has, in comparison to the other two ashes, a different composition. The SiO_2 and the Al_2O_3 content is approx. the half of ash 1. With 28 and 35 wt% FA 6 has a very high amount of calcium oxide. Also the sulphate amount with 4 to 5 wt% is very high. Additionally there are clear differences between batch 1 and batch 2 of this ash.

Requirements according to the standard EN 450-1 (9) are documented in **Table 2**. It can be seen, that fly ashes FA 1 and FA 2 would meet the requirements in the main parts, but fly ash FA 6 not. Based on this fact, it is necessary to mix FA 6 with FA 1 or FA 2 in special ratios. The calculation results are demonstrated also in **Table 2**. For the mortar investigations, two recipes were selected, one recipe for the lab investigations (see **Table 3a**) and another recipe for the field investigations (see **Table 3b**). The lab recipe is a typical one with binder, sand, water and ash only. The field recipe is a common recipe of a plastering and masonry mortar used by the company. Information on the fresh mortar properties can be found in the tables.

Specimens

Mortar bars with a length of 6.30 in. (160 mm) and a width of 1.58 in. (40 mm) were produced. Different tests mentioned above were carried out at these samples. For the color tests, ash powders were stored in a bottle with water and an indicator solution (EDTA according 10). The ultrasonic method was transferred to ash systems. Results, especially ultrasonic curves, are well known with cements and cement-slag-systems (11, 12). For the ultrasonic investigations, ash suspensions with a water/ash ratio of 0.4 were produced and were filled in a special cell. The detectors were adjusted in the sample and the measurement can be realized continuously. The cells are shown in **Fig. 1**. By using this equipment, also the temperature development caused by the reaction of ash samples with water, can be determined. This can be an important tool too to characterize ashes.

Items of investigation

At the age of 7 and 28 days, mortar specimens were tested for compressive strength and bonding strength, respectively. The activity indices were measured after 28 and 90 days. The measurements of the shrinkage, swelling and dynamic modulus of elasticity took place continuously. Also continuously, the measurements of Ultrasonic velocity were realized.

Additionally a temperature curve of each ash-water mixture could be measured.

EXPERIMENTAL RESULTS AND DISCUSSION

Activity indices

According to the standard EN 450-1 an important value to characterize the reactivity of fly ashes or other admixtures is the activity index. It is determined after 28 and 90 days storage under normal conditions (65% r.H., 20°C) in comparison to a sample, where the binder is completely cement. The substitution value is 25 wt% of cement by fly ash. The results are demonstrated in **Fig. 2**. Especially fly ash FA 6 with both batches reaches the minimum values, which is a further reason for their use and a proof for their self-hardening properties.

Shrinkage and swelling behavior

The use of fly ashes, especially with large amounts of CaO (included free CaO) can lead to a swelling process. Maybe also shrinkage can be a problem. Additionally the knowledge of such behavior is important for their practical application. Shrinkage and swelling curves of different fly ashes and also of mixtures and under different conditions (dry, wet) are summarized in **Fig. 3a/b** and **Fig. 4a/b**. It can be seen that the developed compound shows a similar behavior in comparison to the reference ash. With maximum values of 0.6 mm/m the results are in a normal range for mortars. Especially results, measured under wet and dry-wet conditions alternating, give the security for a practical application.

Compressive strength and dynamic modulus of elasticity

The changes of the dynamic modulus of elasticity could be measured continuously. The measured curves are documented in **Fig. 5a/b/c** for the pure ashes as a part of the Lab mortar recipe and in **Fig. 6a/b** for the compounds. All curves have a similar pattern, what indicates that damaging processes do not occur in the mortar structure. If such processes would take place the E-modulus should strongly decrease, which cannot be observed here.

An overview on the compressive strength values reached with pure ashes and with ash compounds is given in **Fig. 7**. There are differences, especially mortar samples produced with fly ash FA 1 and fly ash FA 2 show a lower strength. It is remarkable, that the ash compounds reach the same level as the reference sample, which is a further reason to substitute the common hard coal fly ash by the developed compound.

Workability of fresh mortar recipes using compounds and practical test results

All investigations mentioned above are tests in the Lab. What is about tests in the field? Such investigations were also done. The developed compound materials were tested in a special mortar recipe, fresh mortar properties (workability, consistency, density, water retarding behavior) were determined and also compressive and bonding strength values could be measured after 7 and 28 days. The lower part of **Table 3b** gives the result, **Fig. 8** shows the practical application at a wall and **Fig. 9** summarizes the strength values of the field recipes. Especially personal experiences on the handling of this mortar product, summarized in Table 3b, allow the conclusion, that this new developed compound is well suited as a substitute for previously used hard coal fly ashes.

Accelerated test procedure for ashes

However an important problem still needs to be solved, namely: How can the fluctuations in the compositions and properties of ashes be compensated, which are not certificated.

Such test procedures should not take longer than one day. There are several possibilities but we have concentrated on the fast detection of Calcium oxide by using a color test method and on the continuous tracking of the hardening process by using the ultrasonic method coupled with a temperature tool.

First results of such investigations can be described as follows. **Fig. 10** shows a series of glasses filled with different ashes. For the verification of Calcium, EDTA solution was added. The concentration was chosen for 10 wt% CaO, what is the limit according to the European standard. The color change was realized by using the indicator substance “Eriochrome black”. As it can be seen in the figure, ashes with a CaO content lower than 10 wt% show a mainly blue color, ashes with more than 10 wt% a pink color. This test works with pure ashes and with compounds too, what is important for the application. The reproducibility is 2 wt%, probably enough for the application. The test is very simple and needs no additional chemical methods.

But the fast determination of CaO is not enough for the characterization of ashes. A further tool is the knowledge of the setting and hardening process. Because of different amounts of lime, calcium sulphate (anhydrite) and amorphous, and therefore, reactive phases, a method is sought, which reflects all influences on the hardening process. Such method can be the ultrasonic method, coupled with a temperature measurement system. A special equipment allows measuring the ultrasonic velocitiy and the temperature of water/ashes suspensions continuously, starting with 1 to 2 minutes after mixing. **Fig. 11** shows ultrasonic curves of fly ash 1 and fly ash 6 in different mixtures, **Fig. 12** involves the temperature curves of the same compounds. It can be found, that clear differences in the setting and hardening behavior and in the heat or temperature development can be measured. First results can be given:

Ashes with a high calcium oxide content (free lime content respectively) show a larger temperature at the beginning than ashes with lower CaO. Fly ashes with a higher anhydrite content form more ettringite, which is responsible for the course of the first part (asymptotic course) of the velocity curve. The second increase is determined by the formation of amorphous CSH/CAH-phases as a result of the hydraulic reaction of such fly ashes.

The results allow the conclusion, that ashes and ash compounds with different compositions can be distinguished. The method used is also simple, can be easily performed und provides representative results in a short time.

SUMMARY AND CONCLUSIONS

Based on the results of this experimental investigation, the following conclusions are drawn:

1. Lignite coal fly ashes with a high CaO content in general are well suited as a substitute of common hard coal fly ashes in mortar recipes because of their properties. Unfortunately, the compositions do not always meet the normative requirements.
2. However this can be changed by mixing different ashes under consideration of certain limits (CaO content, sulphate amount, sum of SiO_2, Al_2O_3 and Fe_2O_3).
3. Such produced mixtures can have the same or often better properties in comparison to common and previously used ash materials. In cooperation with a company, meaningful applications could be developed.
4. A problem with fluctuations in ash properties from batch to batch exist, which can be solved using a combination of accelerated test methods.
5. A special developed color test allows determining the CaO content in a range of 2 wt%. Continuous measurements of the setting and hardening process using an Ultrasonic method coupled with a temperature measurement system give typical curves for each ash and each compound. Both methods in combination should make sure, that fluctuations between ashes could be balanced.

FURTHER RESEARCH

The accelerated test methods described in the paper will be transferred to other batches of fly ashes to check the procedure for each ash.

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REFERENCES

1. Piekos, S.; Lemke, D., “Physical properties and chemical composition of lignite coal fly ashes“, *Manual of the utilization of lignite coal fly ashes in Germany,* RWE-Company for Research and Development, Wesseling, 1995, pp. 71-86 (in german).

2. Blissett, R. S.; Rowson, N. A., “A review of the multi-component utilization of coal fly ash”, *Fuel,* Vol. 97, 2012, pp. 1-233.

3. Ahmaruzzaman, M., “A review on the utilization of fly ash”, *Progress in Energy and Combustion Science,* Vol. 36, 2010, pp. 327-363.

4. Dietz, S., “Mineralogical, chemical and technological properties of lignite coal fly ash – cement – systems“, PhD-Thesis, Univ. Heidelberg, 1996, 227 pp. (in german).

5. Mallmann, R., „Development of hydraulic binders with Rhenish lignite coal fly ashes“, PhD Thesis, Univ. Siegen (Germany), 2002, 175 pp. (in german).

6. Meißner, M.; Backes, H.-P.; Brandenburger, D., „Fly ash - availability, logistics, potentials,“ BauMineral GmbH Herten, 2011, 23 pp. (in german).

7. Turgut, P., “Masonry composite material made of limestone powder and fly ash”, *Powder Technology,* Vol. 204, 2010, pp. 42-47.

8. Sathonsaowaphak, A., Chindaprasirt, P., Pimraksa, K., “Workability and strength of lignite bottom ash geopolymer mortar”, *Journal of hazardous Materials,* Vol. 168, 2009, pp. 44-50.

9. DIN EN 450-1, „Fly ash for concrete“, Deutsches Institut für Normung e.V., 2012, pp. 6.

10. www.mtsu.edu/chemistry/chem2230/pdfs/Exp9A.pdf, “Determination of calcium by Standardized EDTA Solution”, found 01-26-17.

11. Carette, J.; Staquet, St., “Monitoring the setting process of mortars by ultrasonic P and S-wave transmission velocity measurement”, *Construction and Building Materials*, Vol. 94, 2015, pp.196-208.

12. Robeysta, N.; Gruyaerta, E.; Grosse, C.-U.; De Belie, N., “Monitoring the setting of concrete containing blast-furnace slag by measuring the ultrasonic p-wave velocity”, *Cement and Concrete Research*, Vol. 38, 2008, pp. 1169-1176.

13. Burri, C., „Petrochemische Berechnungsmethoden auf äquivalenter Grundlage (Methoden von Paul Niggli)“. Birkhäuser Verlag, Basel, Stuttgart, 1959, pp. 47-103.

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Table 1–Chemical and mineralogical composition of fly ashes

Chemistry/Mineralogy	Fly ash 1 FA 1 (Poc)		Fly ash 2 FA 2 (Vres)		Fly ash 6 FA 6 (Che)	
	batch 1	batch 2	batch 1	batch 2	batch 1	batch 2
SiO_2 (S)	59.81	60.5	48.58	50.32	37.67	28.99
Al_2O_3 (A)	29.42	29.87	29.65	30.81	14.67	15.03
Fe_2O_3 (F)	4.82	4.19	8.63	8.38	10.55	11.09
CaO	1.39	1.43	2.08	2.39	28.62	35.53
SO_3	0.13	0.15	0.26	0.29	4.16	5.37
Quartz	9	9	8	8,5	18	14
Anhydrite ($CaSO_4$)	1,5	1,5	1	2	6	8
Mullite	46	44	57	46		
Brownmill. ($C_2(A,F)$)					17	15
amorphous	38	41	24	34	29	35
Lime (CaO_{free})					6	7
Gehlenite (C_2AS)					8	5
Composition amorphous based on NIGGLI calculations (13)	15% Al_2O_3 85% SiO_2	17% Al_2O_3 83% SiO_2	5% Al_2O_3 95% SiO_2	24% Al_2O_3 76% SiO_2	14% Al_2O_3 68% SiO_2 18%CaO	22% Al_2O_3 42% SiO_2 36% CaO
Remarks	No significant fluctuations between batches		Chemically almost identical composition. Mineralogical differences in mullite content and amorphous content + their composition		Clear differences in chemistry and mineralogy	

Table 2–Requirements according to EN 450-1 and ratios

Components	Fly ash 1 (Poc)		Fly ash 6 (Che)		Ratio ba.1	Ratio ba.2	Requirements	
	batch 1	batch 2	batch 1	batch 2	70/30	75/25	EN 450-1 [wt%]	
S+A+F	94.05	94.56	62.89	55.11	84.70	84.69	>=	**70.0**
SO_3	0.13	0.15	4.16	5.37	1.34	1.46	<=	**3.0**
CaO whole	1.39	1.43	28.62	35.53	9.56	9.96	<=	**10.0**

Table 3a–Mortar recipe (Lab) and consistency

Components [g]	**Reference**	**Compound FA1/FA6 70/30**
Cement CEM II / A-LL 32.5 R	218	218
Limestone	152	152
Sand 0-2mm	1458	1458
Hard coal fly ash Opole	170	
Fly ash 1 ba.1		119
Fly ash 6 ba. 1		51
Additive MC cellulose	0.6	0.05
Water	360	345
Sum	2358.6	2343.05
Fresh mortar properties		
Consistency in mm	160	160

Table 3b–Mortar recipe (Field) and fresh mortar properties

Components [in g]	Reference	Compound FA1/FA6
CEM II / A-LL 32.5 R	65	65
limestone	45	45
Sand 1-2mm	50	50
lime hydrate	20	20
hard coal fly ash Op (reference ash)	70	
Compound FA 1 ba.1 + FA 6 ba. 1 70/30		70
Sand 0-1	750	750
additive LP 50	0,05	0,05
additive Culminal 8350	0,2	0,2
additive Ferrogranul	0,18	0,18
sum	1000,43	1000,43
fresh mortar properties		
water/solid ratio	0,175	0,16
mixing time	15/30	15/30
consistency in mm	180	172
fresh mortar density in kg/l	1,983	1,855
air content in %	7,2	12
water retarding in %	75,5	71,5
fertility in l/t	593	625

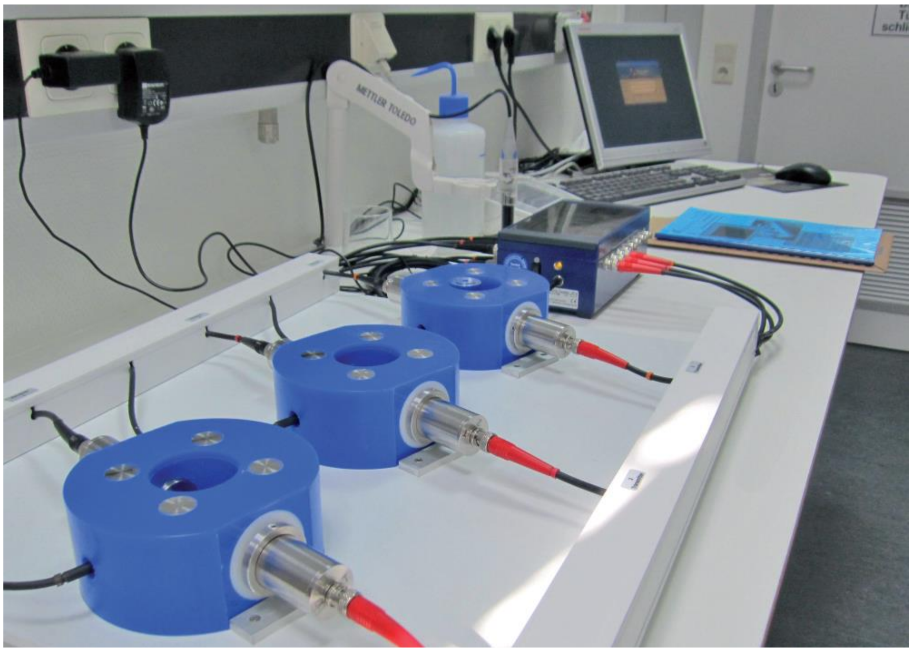

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Fig. 2 -Activity indices of fly ashes investigated after 28 d and 90 d hardening process

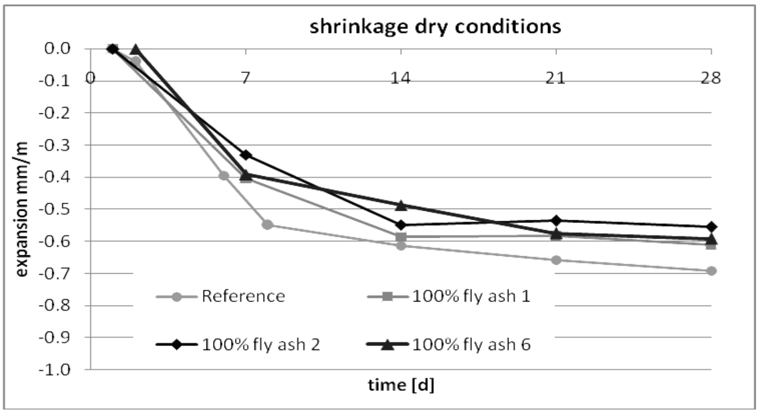

Fig. 3a – Shrinkage during dry storage [1 mm = 0.04 in.]

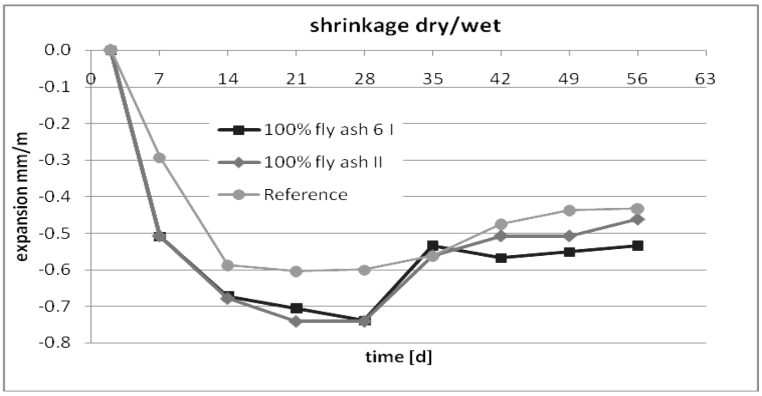

Fig. 3b – Shrinkage during dry/wet storage [1 mm = 0.04 in.]

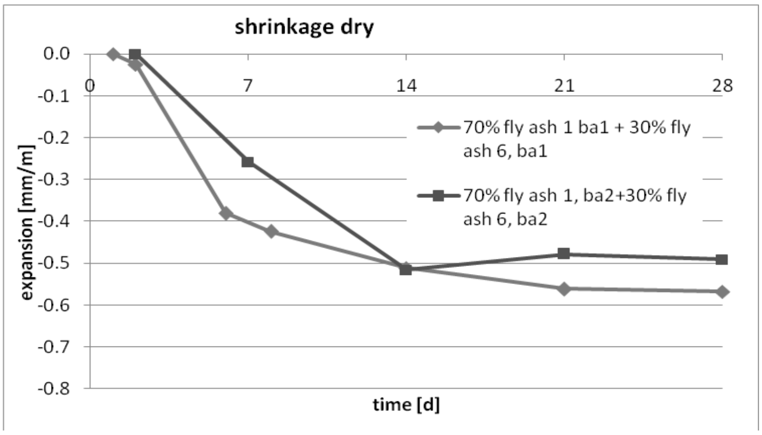

Fig. 4a – Shrinkage of compounds under dry conditions [1 mm = 0.04 in.]

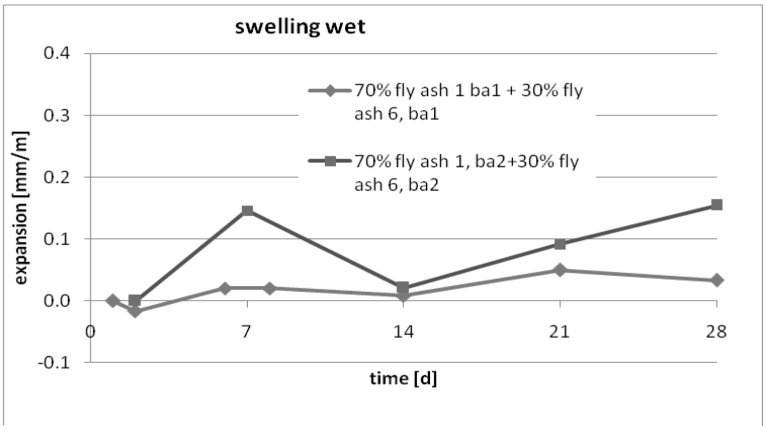

Fig. 4b –Swelling of compounds under wet conditions [1 mm = 0.04 in.]

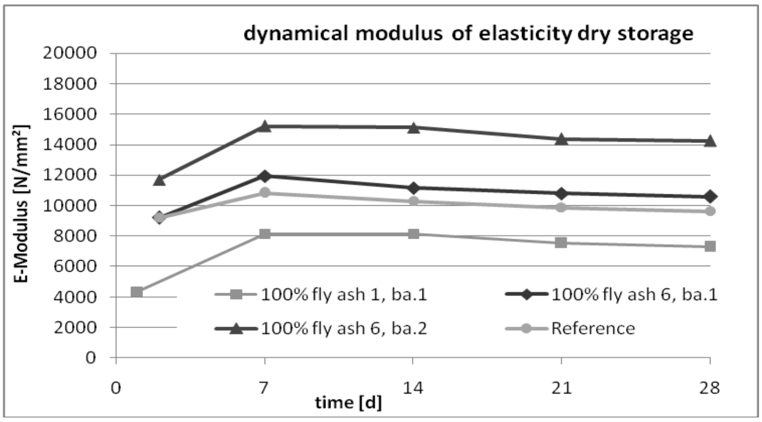

Fig. 5a – Dynamic modulus of elasticity of ashes under dry conditions [1 N/mm^2=1 MPa]

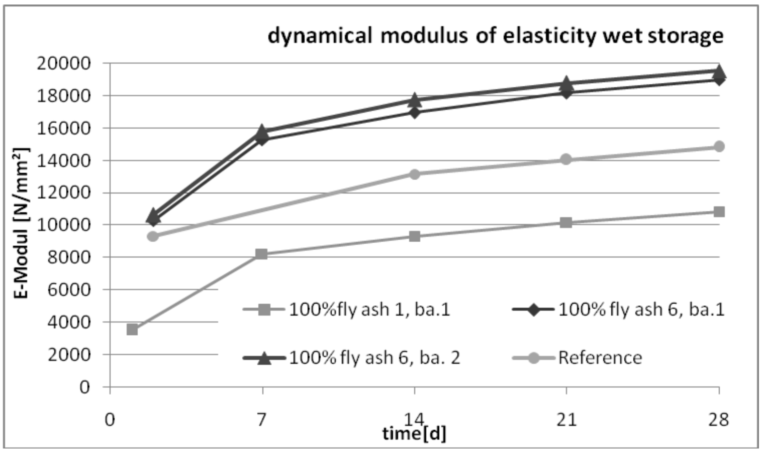

Fig. 5b – Dynamic modulus of elasticity of ashes under wet conditions [N/mm^2=MPa]

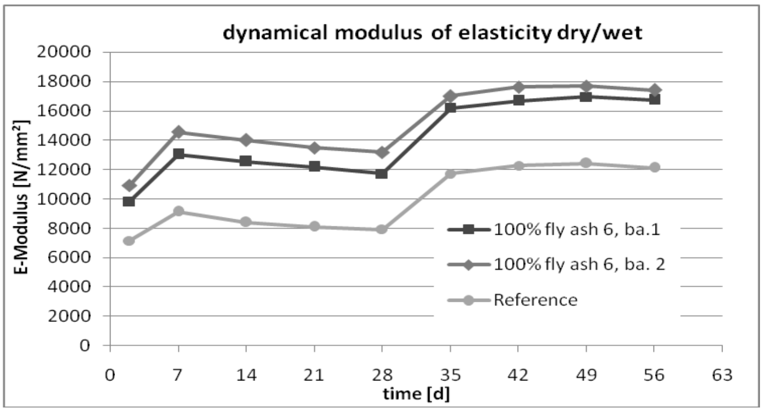

Fig. 5c – Dynamic modulus of elasticity of ashes under dry/wet conditions [N/mm^2=MPa]

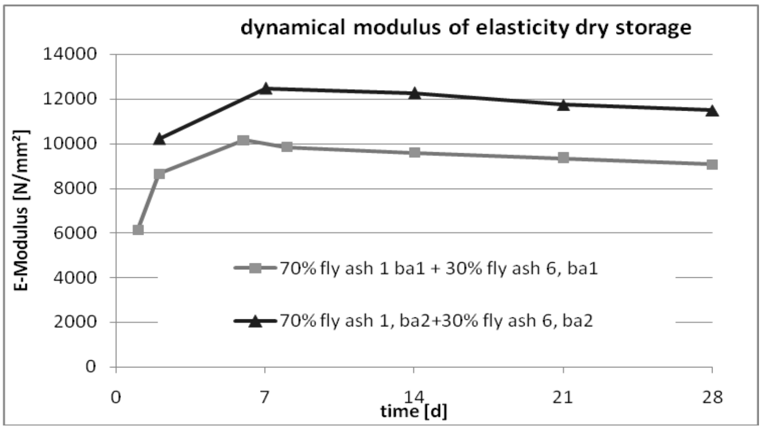

Fig. 6a –Dynamic modulus of elasticity of compounds under dry conditions [N/mm^2=MPa]

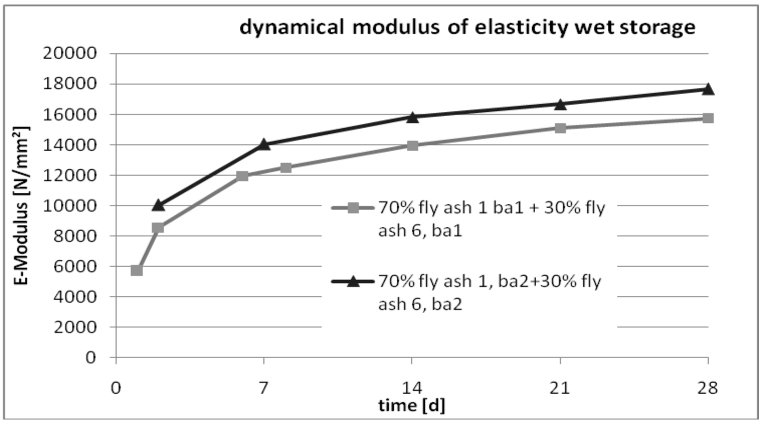

Fig. 6b – Dynamic modulus of elasticity of compounds under wet conditions [N/mm^2=MPa]

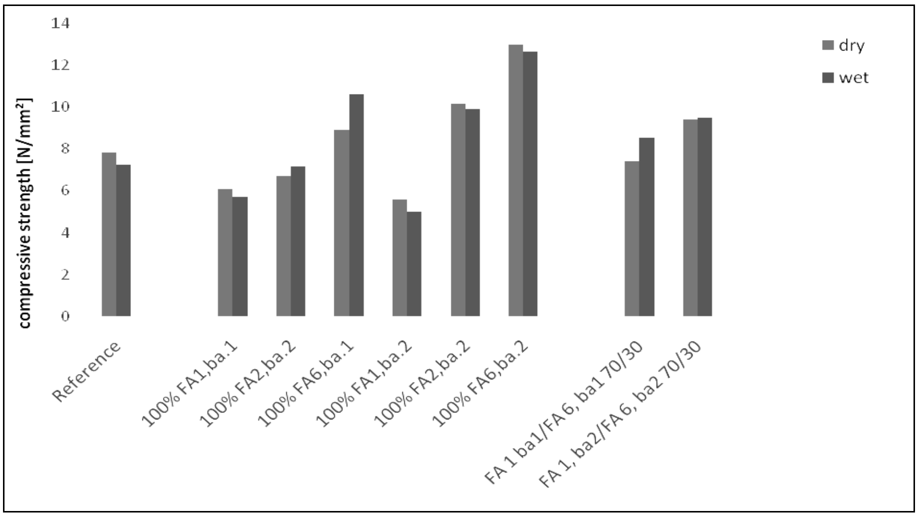

Fig. 7 – Compressive strength of ashes and compounds of Lab recipes [N/mm^2=MPa]

Fig. 8 – Test of bonding strength & detail of the compound mortar placed on a wall (photo: SAKRET Trockenbaustoffe Sachsen GmbH & Co. KG, Gewerbepark Diethensdorf 1, 09236 Claußnitz, Germany)

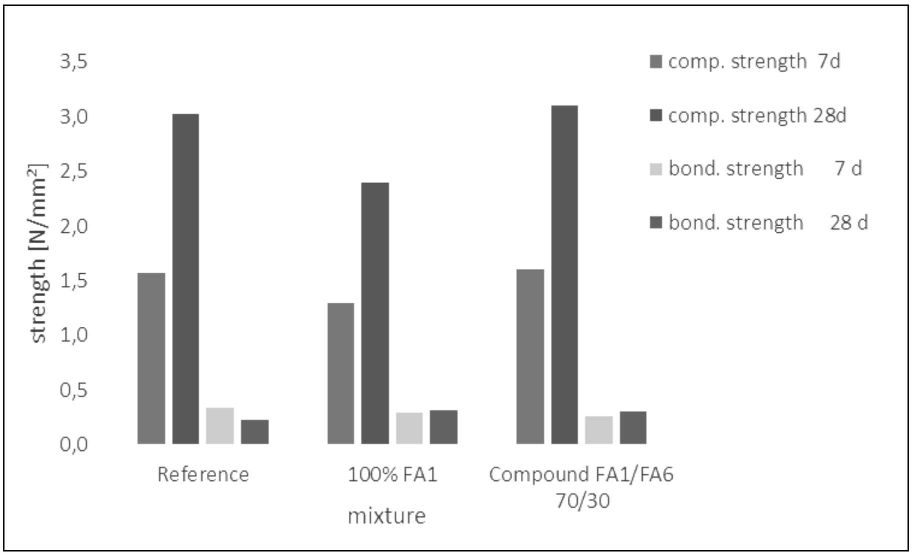

Fig. 9 – Comparison of recipes chosen: Reference&Compound 70/30 for a plastering mortar [1 N/mm^2=1 MPa]

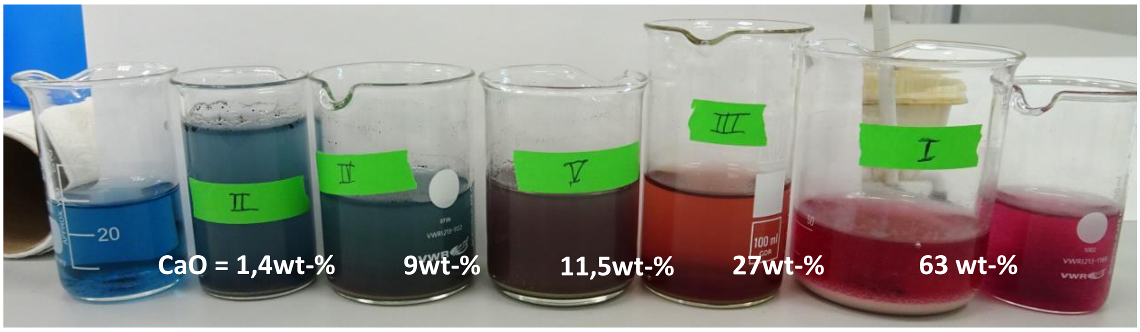

Fig. 10 – Different colors caused by different CaO contents of fly ashes

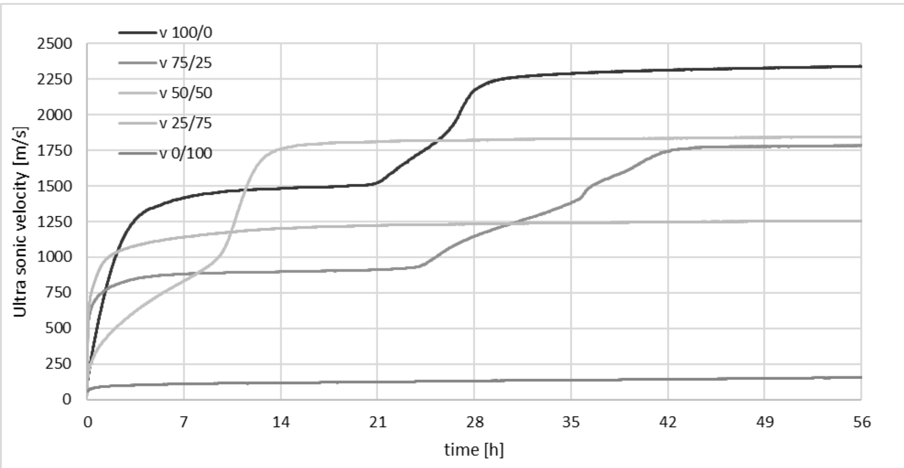

Fig. 11 – Results of ultrasonic investigations (velocity) of different FA compounds [1 m=39.75 in.]

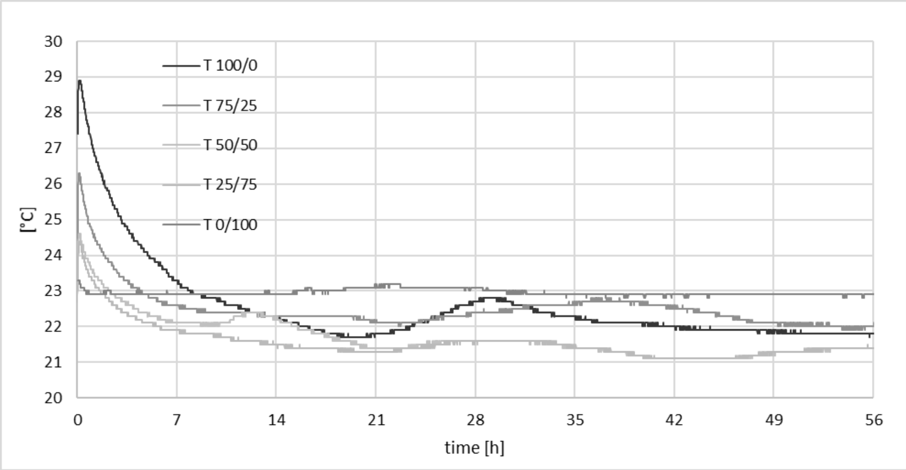

Fig. 12 – Results of temperature measurements of different FA compounds