ONLY PRECISE DOCUMENTATION OF THE MATERIAL PREPARATION CONDITIONS LEADS TO REPRODUCIBLE AND TRACEABLE RESULTS IN THE RESEARCH OF REFRACTORY CASTABLES

Olaf Krause[1], Johannes Kasper[2], Daniel Tischer[3], Florian Holleyn[1], Christian Dannert[2]
[1]Hochschule Koblenz, Höhr-Grenzhausen, Germany;
[2]Forschungsgemeinschaft Feuerfest e. V., Höhr-Grenzhausen, Germany;
[3]Mineralwerk Westerwald Horn GmbH & Co. KG, Weitefeld, Germany;

ABSTRACT

This article contributes to a better understanding how sample preparation influences technological parameters. Over the last ten years' research in the field of rheology, setting and curing behaviour and strength evolution clearly shows that the obtainable results are strongly dependent on the sample preparation conditions. Firstly, the flow properties of refractory castable are not only affected by the water addition but also by the mixing conditions. Imprecise adjustments of the power input significantly change the flow properties and in consequence the densification of the material. On the one hand for material development in the laboratory this requires mixing devices where the mixing energy input can be monitored and adjusted precisely at least for the set of samples prepared for a single material development. On the other hand, mixing conditions on site should be checked carefully because it is common knowledge that the mixing devices available in the user's industry often do not cover the requirements for a proper mixing of highly dispersed refractory castables therefore castables will behave different.

In principle, it is not necessary to mention that curing time and ambient curing conditions impact the technological properties measured thereafter. However, it is worth to mention that even small deviations of the curing conditions show a strong impact on the results. Special care must be taken with regard towards the relative ambient humidity. Even if the relative humidity is adjusted to 95 % as recommended by ISO 1927 a significant loss of pore water is recordable. Less pore water leads to a significant increase of the green strength. It is highly recommended to adjust not only the curing temperature but also the prevailing relative humidity because it affects the dry-out behaviour over the curing time. At this point it is important to reflect the mixing conditions again, because at this early stage of preparation this high-energy input changes the temperature of the admixture and already leads to a significant loss of mixing water.

In this article, we will demonstrate and conclude that reliable and reproducible results can only be obtained if all preparation parameters are adjusted to constant conditions and points out that only proper documentation will lead to transparent results. This is necessary for a stringent material development in a laboratory and should also be part of every publication in the refractory castable research.

INTRODUCTION

It is not necessary to depict the advantages of monolithic refractory materials due to their universal possibilities in thermal loaded industrial devices. Their rapid installation properties and their infinite possibilities of shaping speaks for their favour.

However, in comparison to refractory brick, monolithic materials must be processed to sample specimens by moulding prior to the standardized technological testing. The moulding of specimens plays a pivot role for a proper data acquisition for both material development and quality control. In contrast to fired refractory brick that are typically pressed and thermal treated at precisely defined conditions the technological properties of monolithics depend strongly on the preparation conditions [1, 2, 3]. They are responsible for the densification and homogeneity of the material. The densification properties of monolithics are dependent on the rheological properties during casting that are for their part dependent on the mixing energy, the precise dosage of dispersants and the water addition. Even small changes will significantly affect the flow properties during casting [4]. In further the setting and curing time which are dependent on the ambient conditions (temperature and relative humidity) influence the strength evolution of the casted specimens. This is especially true for the green strength but also visible in samples that are in a dried stage at 100 °C. To obtain comparable results, it is very important that technological measurements are carried out after precisely defined preparation parameters, curing time and ambient condition [5]. For the measurement of strength ISO 1927 recommends four sample formats (A to D) that significantly vary in their dimensions. ASTM and Australian Standard (AS) again provide their own shapes. In principle, it is not worth to mention but beside all imponderabilia listed above, bigger sample sizes systematically lead to lower strength values [6].

The results presented in this article are derived from two research projects and clearly demonstrate that even minor changes in the sample preparation process significantly influence the results which are then no longer comparable.

GENERAL METHODS

All presented results refer to a model castable composition as it is shown in tab. 1. The amount of water and dispersant addition were altered as explained in the results. The tests were carried out by using an EIRICH R05 mixing device that can apply different mixing conditions that allow to change the mixing energy input into the castable. During mixing the engine power was recorded to determine the power input and the progression of the mixing process. A pin and a star mixing tool were used and in addition the mixing time for dry and wet mixing were altered.

Table 1: Composition of the refractory model castable

components	weight /%
tabular alumina 0-6 mm	77
reactive alumina	18
CAC (70 weight percent Al_2O_3)	5
sum	**100**
water	variable
dispersing agent PCE	variable

The rheological properties of the resulting self-flowing castables were analysed by applying a ball measuring system (BMS, Schleibinger ViskomatNT) (reported in [1]) and a time resolved slump-flow test according to Klein et al. [7].

The curing conditions (temperature and relative humidity) were kept constant at 20 °C and relative humidity of 95 % in a climate cabinet.

Furthermore, the cold crushing strength and cold bending strength at green state and after drying at 100 °C were measured in accordance to ISO 1927-6.

RESULTS

Influence of the energy input during wet mixing and impeller design

Fig. 1 to Fig. 5 demonstrate the influence of the impeller design (pin and star), the relative movement of the impeller to the mixing bowl (cross-flow and concurrent flow) and the mixing time on the workability and the strength evolution. In dependence on the mixing velocity the mixing time was adjusted for every mix where a constant power input of the mixing device indicates homogenization of the mix.

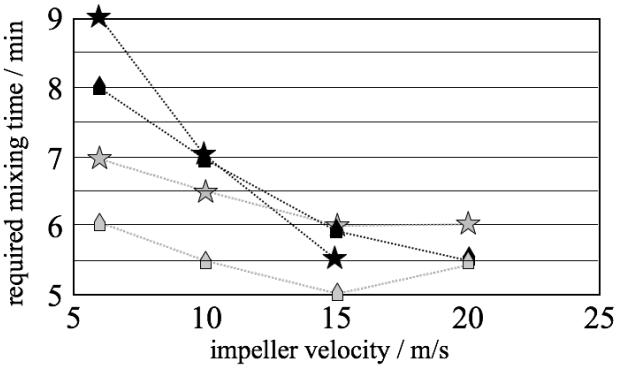

Fig. 1: Required mixing times as a function of impeller velocity, impeller design and relative movement of impeller and bowl. The symbols are related as follows: ⬮ pin concurrent flow; ★ star concurrent flow; ⏢ pin cross-flow; ☆ cross-flow.

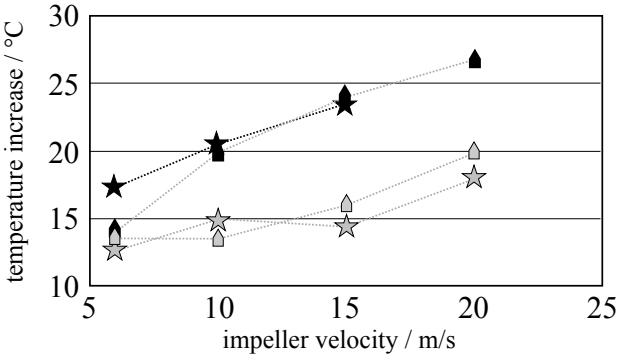

Fig. 2: Temperature development during mixing as a function of impeller velocity, impeller design and relative movement of impeller and bowl. The symbols are related as listed in Fig. 1.

As indicated in Fig. 1, the homogenization is achieved earlier with increasing impeller velocity. This is of course not very surprising, because the energy density is higher at higher mixing velocities. However, it remains remarkable that the required mixing time varies in a wide range between 5.5 and 9 minutes. In further the design of the impeller and the relative movement of the bowl and the impeller strongly affects the required mixing time. A pin agitator in concurrent flow direction to the bowl leads to highest efficiency due to the shortest mixing time over all experiments. The slump flow as envisaged in Fig. 3 shows better flow for cross-flow conditions, due to less warming of the mix and less dry-out during slump-flow measurement. However, as indicated by the modulus of rupture (Fig. 4) and cold crushing strength (Fig. 5), the cross-flow agitation does not lead to the best results for the said parameters. The reason for this on the first glance unexpected result is visible during the mixing process under cross-flow conditions. Here the material appears more swirled and more air is intermixed into the mixture. This material air intermixture leads to an apparent homogenization indicated by a constant power input the mixing device indicating an already homogenised material.

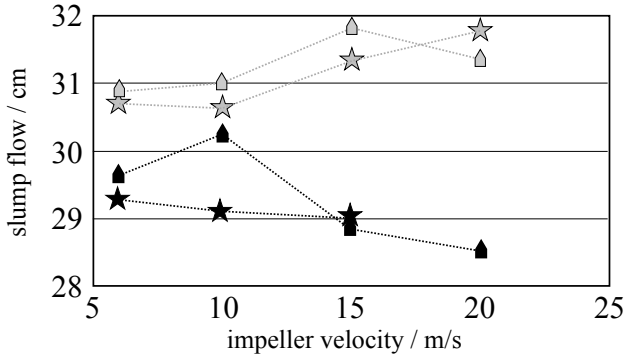

Fig. 3: Slump flow 10 minutes after mixing as a function of impeller velocity, impeller design and relative movement of impeller and bowl. The symbols are related as listed in Fig. 1.

In principle, higher mixing velocities lead to higher temperatures in the mixes due to the higher friction energy that incurs between particles. Fig. 2 shows that the temperature shift beginning from 20 °C lies between 12 and 26 °C, whereat cross-flow agitation leads to significant lower temperature increase. This can be explained with a lower inter-particle friction because the material is swirled in the entire mixing bowl volume.

The temperature increase affects the workability of the castables. As envisaged in Fig. 3 castables that obtained a higher heat gain show lower slump flow values. This could be correlated with the specific character of the slump-flow test, because of the high surface area at the end of the measurement where more water can be evaporated. This has to be allocated to the specific measurement conditions of the slump-flow test and could not be approved by further rheological tests [1].

Best slump flow values do not indicate best mechanical strengths after drying at 100 °C. For both cold modulus of rupture (Fig. 4) and cold crushing strength (Fig. 5) it shows that a pin agitator leads to higher strength values. This general tendency is getting more pronounced with increasing impeller velocity. While at a mixing speed of 6 m/s all mixing-attempts lie between 11.4 and 13,3 MPa for modulus of rupture and 74.6 and 80.8 MPa for cold crushing strength, the gap increases strongly at higher impeller velocities. The modulus of rupture show values between 12 and 16.6 MPa and cold crushing strength between 74,7 and 106,7 MPa.

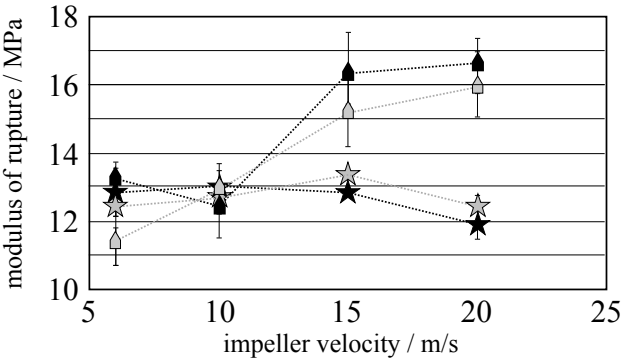

Fig. 4: Cold modulus of rupture development during mixing as a function of impeller velocity, impeller design and relative movement of impeller and bowl. The symbols are related as listed in Fig. 1.

Influence of the moulding temperature on the mechanical strength

Even if the mixing parameters are kept constant the temperature of the admixture can vary significantly if the raw materials and the mixing water have a variable temperature due to storage under cool or warm temperatures. Fig. 6 and Fig. 7 demonstrate for two different mixing conditions how the resulting strength is influenced.

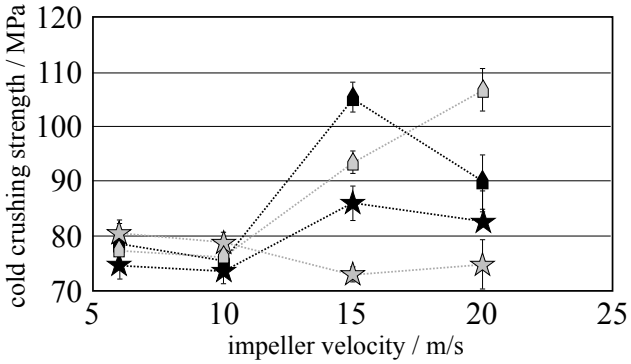

Fig. 5: Cold crushing strength development during mixing as a function of impeller velocity, impeller design and relative movement of impeller and bowl. The symbols are related as listed in Fig. 1.

In the first set of castables the mixing speed was set to 6 m/s, mixing time to 8 minutes and starting temperatures varied from 20 °C to 30 °C. The second set was mixed with 20 m/s for 5,5 minutes, Here the starting temperature was fixed to 2,2 °C and 18,5 °C. The resulting temperatures can be read out of the diagrame.

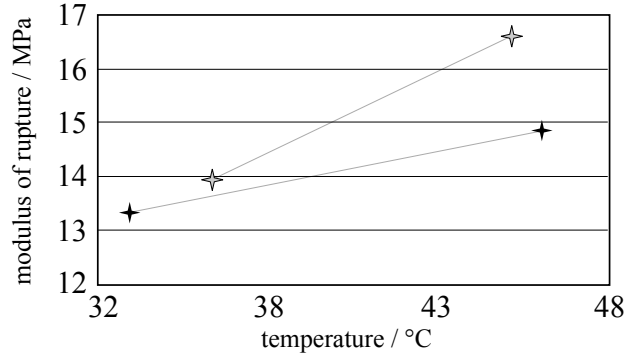

Fig. 6: Strength increase of modulus of rupture as a function of moulding temperature. The symbols are related as follows: ✦ mixing speed, 6 m/s, mixing time 8 min; ✧ mixing speed 20 m/s; mixing time 5,5 min

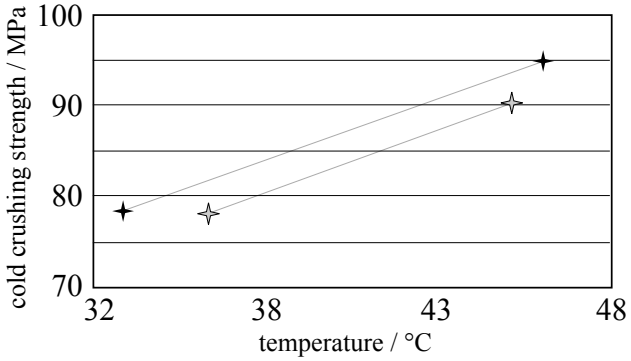

Fig. 7: Strength increase of cold crushing strength as a function of moulding temperature. The symbols are related as listed in Fig. 6.

In principle, it is not worth to mention that higher starting temperatures lead to higher temperatures of the mix at the end of the mixing process. For both mixing conditions the obtained strength significantly increases with the temperature whereat this effect is more pronounced for the cold crushing strength.

There is some indication thatat higher end temperatures for the mixing process more water is evaporated and therefore material gets more dense because of less remaining pore water. In further it has to betaken into account that the setting velocity is of course higher for the mixes with higher moulding temperature. If castables start to harden earlier, a longer curing period is available between moulding and testing. According to ISO 1927 physical testing after 100 °C has to be initiated 72 hours (24 h curing in the mould, 24 h curing after demoulding and 24 h in the dryer).

Influence of the dispersant and mixing water addition

Marginal changes in the dispersant and mixing water content cause significant changes for the resulting strengths after drying at 100 °C. Within a range of 0.07 and 0.20 wt.-% of dispersant addition the cold crushing strength drops from 113 to 83 MPa and the modulus of rupture is decreased from 14 to 12 MPa.

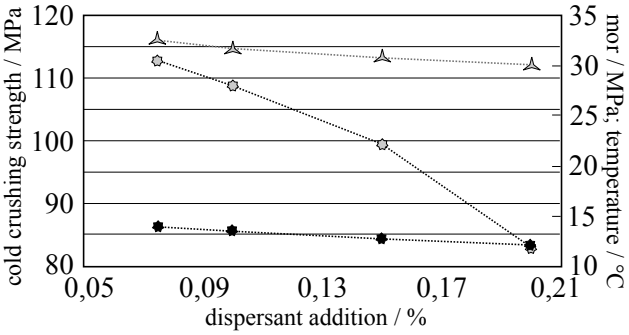

Fig. 8: Temperature after mixing (⅄), cold crushing strength (✹) and cold modulus of rupture (✹) as a function of dispersant addition.

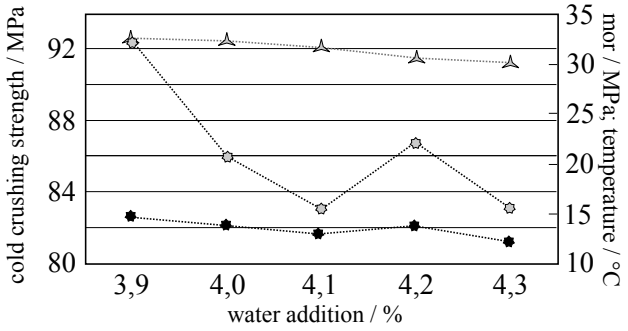

Fig. 9: Temperature after mixing (⅄), cold crushing strength (✹) and cold modulus of rupture (✹) as a function of mixing water addition.

Similar results are obtained if the mixing water concentration is increased from 3,9 to 4,3. Here the cold crushing strength declines from 93 to 83 MPa and the modulus of rupture is reduced from 15 to 12 MPa. The increase of dispersant and mixing water in the said range can be undesirably achieved if mixing does not lead to an adequate homogenization of the dispersant or unwanted water vaporization if the mixing temperature is increased significantly by inter-particle friction. Fig. 8 and Fig. 9 show that changes in the dispersant and water addition affects the temperature measured after mixing within 2 °C. As it was also visible in Fig. 2 to Fig. 9 the mixing end-temperature correlates positively with the strength. Therefore, it is highly recommended that the temperatures are accurately documented prior as well as after the mixing process. Otherwise it turns almost impossible to compare results of different development steps in castable development.

Green strength evolution and the role of pore water

Fig. 10 shows the early green strength evolution in castables between the 12th and the 48th hour. All results were derived from sample specimens made in a single mix. It is easy to identify two sets of strengths that can be distinguished in a set of samples that contain pore water and samples where the pore water was removed by the freeze-drying method that was already reported by Krause et al. [5]. It is easy to conclude that in the shown case the total removal of pore water causes a strength increase by 75 %. Therefore, if green strength is an analytical parameter, the

ambient conditions during the curing period of castables is very important. A relative humidity of 95 % already causes an evaporation of residual pore water. Consequently, time-related strength increases are not only caused by the curing of the cement hydrate phases but also by pore water release.

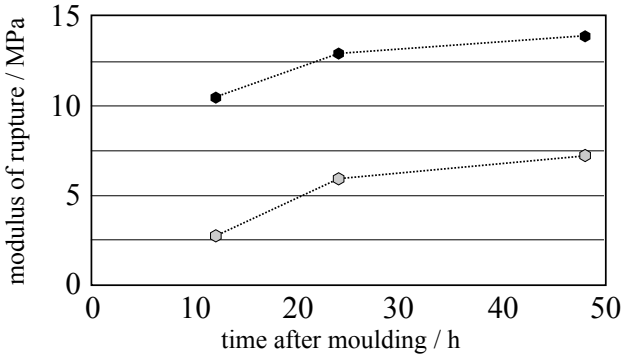

Fig. 10: Evolution of green modulus of rupture for freeze dried, pore water free (⬢) and pore water containing castables (⬡) as a function of time after moulding (12 to 48 hours).

The effect of sample dimension on technological properties

It is common knowledge and already stated by Krause and Krebs in 2008 that the specimen size is of great importance if technological properties are compared [6] for acceptance certificates or from different sources in literature. In the context of this article it is worth to mention the dependence of the technological results on the specimen size once again.

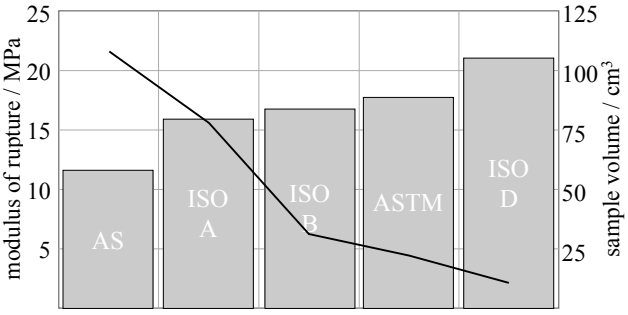

Fig. 11: Cold modulus of rupture as a function of sample volume derived from a MCC castable as reported in [6].

CONCLUSION

This article highlights some aspects that influence the properties of castables. In particular the mixing process leads to a large variation of results if the mixing power is not precisely defined. The reason was already reported by Pileggi et al. [8, 9]. They state that mixing is substantially necessary to deagglomerate even the fine matrix components. This is necessary to achieve a good flow of the castables during moulding. Schmidtmeier et al. summarize the importance of reproducible testing conditions in terms of repeatable cement hydration and setting reaction. Water should be in excess in the formulation and the temperature conditions should be kept as constant as possible. If the research is focused on the cement reaction, they propose to use a standard test grog with defined particle size distribution and cement content. In further Schmidtmeier et al. state that the storage conditions during setting and curing significantly influence the strength evolution in the castables [10].

From the viewpoint of our research we would amend that the mixing parameters are the linchpin for reproducible results. In particular the heat absorption during mixing causes different initial conditions for the early cement hydration. Higher temperatures firstly lead to an accelerated cement reaction and secondly the effect of a higher evaporation rate of mixing water should be analysed deeper in the future. Both lead to higher strengths typically determined after 48 hours. The initial temperature condition after mixing significantly affects the entire setting and curing period even if the setting and curing conditions are precisely adjusted after mixing. Heat absorption during mixing depends on inter-particle friction and friction caused by the mixing device. This effect is significantly higher if the particle shapes tend to interlock and the flowability is reduced due to a lack of mixing water and/or dispersing agent.

This recent research work highlights that there is still a lack of knowledge about the early cement reaction in terms of the strength evolution of castables. In principle the ambient conditions, the influence of the mixing process and the role of mixing water play an important sensitive role. For a comprehensible castable development and quality control it is therefore necessary to document the preparation parameters in more detail. Especially the initial temperature of the mix, the temperature after mixing and lay the foundation for the material properties. They significantly influence the castable properties.

ACKNOWLEDGEMENT

This study was financially supported by “Stiftung Rheinland-Pfalz für Innovation” (grant-number 961-386261/1026) and the German Federation of Industrial Research Associations (AiF) for its financial support of the research project IGF-No. 119 EN. The latter project was carried out under the auspices of AiF and nanced within the budget of the Federal Ministry of Economics and Technology (BMWi) through the programme to promote collective industrial research (IGF).

REFERENCES

[1] Kasper, J. and Krause O. Mixing optimization of an alumina based LC-castable by applying variable power inputs, Unitecr 2013, Victoria, Kanada, proc. p. 941-946

[2] Krause, O., Klein, T., Tischer, D., Schwarz, K., Kasper, J. Setting velocity of cement pastes and monolithics–the impact of mixing. REFRA&HITHERM Prague, 2014, proc. p. 179-185

[3] Kasper, J., Krause, O. Mixing optimization of an alumina based LC-castable by applying variable power inputs in Calcium Aluminates - Proceeding of the International Conference 2014, ISBN 978-1-84806- 316-7, IHS BRE Press, proc. p. 450-456

[4] Halapa, V., Marjerrison, J., Martin-Calle, S. The importance of test piece preparation of unshaped refractory products for the characterisation of physical properties according to EN ISO Standards, 2015 refractory worldforum, 7, p. 73-80

[5] Krause, O., Tischer, D., Kasper, J., Dannert, C. The influence of the water-to-cement ratio on the formation of CA hydrate phases in refractory castables after water addition 59th Int. Coll. On Refractories, Aachen 2016 proc. p. 148-151

[6] Krause, O., Krebs, R. Test procedures for unshaped refractories under the aspect of globalization 51th Int. Coll. On Refractories, Aachen 2008 proc. p. 49-52

[7] Klein, L., Krause, O. Automatic image analysis of slump flow and comparison to rheological measurements with the ball measuring system. 59th Int. Coll. On Refractories, Aachen 2016 proc. p. 155-158

[8] Pileggi R. G., Studart A. R., Pandolfelli V. C., Gallo J. B. How mixing affects the rheology of refractory castables, part 1, 2001, American Ceramic Bulletin 6/80, 27–31

[9] Pileggi R. G., Studart A. R., Pandolfelli V. C.: „How mixing effects the rheology of refractory castables, part 2, 2001, American Ceramic Bulletin, 7/80, 38–42

[10] Schmidtmeier, D.; Buhr, A.; Wams, G.; Kuiper, S.; Klaus, S.; Götz-Neunhoeffer, F.; Zacherl, D.: “Cement Hydration and strength development – how can reproducible results be achieved? Part I+II”, Unitecr’13, Victoria, Canada, 2013.