

# Alternative Evaluation of the grindability of Pozzolan Materials for Cement Production

**K Dvořák and D Dolák**

Brno University of Technology, Faculty of Civil Engineering, Veveří 331/95, 602 00  
Brno, Czech Republic

E-mail: dolak.d@fce.vutbr.cz

**Abstract.** An ecological way of reducing CO<sub>2</sub> emissions in cement production is the usage of blended cement with an active pozzolan. A part of this issue is the adjustment of granularity of raw materials. This is often achieved by the grinding of the input components. All conventional methods for the evaluation of grindability require a specific grinding instrument. These grinding instruments do not have any other practical use and thus are not very common. This paper focuses on the alternative evaluation of grindability. Inspired by the VTI method used in the coal industry, which uses porcelain laboratory ball mill and compares material based of oversize particles, a new method was created. The first modification in methodology was the use of a planetary mill instead of a porcelain drum mill. Another modification was in the measurement of undersize by means of laser granulometry. This method was then tested on clinker, slag, and recycled glass, which can also be used as an active pozzolan in blended cement. Also, co-milling measurements were made on clinker-pozzolan combinations. These results were then used in the calculation of the grindability index, which can be used for the comparison of properties. The modification of the VTI methodology has a positive impact on the evaluation of grindability, especially with regard to fine particles, thanks to the use of laser granulometry and at the same time it makes use of more a commonly available grinding apparatus

## 1. Introduction

The cement industry produces a large amount of CO<sub>2</sub>. Eight percent of global CO<sub>2</sub> emissions can be attributed to the production of cement. Half of this amount is produced by fuel combustion while the other half is from non-combustion sources [1]. For every ton of cement, approximately half a ton of CO<sub>2</sub> is produced. This is also the reason for the increasingly stricter requirements on the usage of waste products as secondary raw materials. One way to reduce CO<sub>2</sub> emissions in cement production is the use of alternative fuels. Another possibility is the production of blended cement, to which latent hydraulic, pozzolan or even inert materials are added [2]. In this way, CO<sub>2</sub> emissions are reduced by 10 to 15% [3]. Since these materials are often added to cement after firing, i.e. during the homogenization process, a part of this issue is the modification and grinding of materials.

Larger particles tend to disintegrate sooner in the grinding process and with less milling energy. The difference in the speed of decreases in the size of particles from various materials can be explained by the differences in their mechanical properties [4]. During grinding, external forces are applied to overcome the cohesion forces between the molecules in the material being ground. This causes disruption of the grains. This disintegration results in an increase of the total specific surface area. As a result of cracks, fissures, and some non-homogenous surface areas, the actual technical strength is much



smaller than the theoretical molecular strength. During grinding, individual particles disintegrate in areas of diminished strength. When the particle size is reduced further, the number of such areas gradually decreases, and this increases their resistance to further disintegration. This is one of the main causes of the high specific energy consumption in fine particle grinding [5].

One of the major technological tests for ascertaining whether a material is suitable for technical practice is the test of grindability. Grindability represents a relative value that expresses by how much the grinding effect of the test substance differs from the standard. Grindability can be defined as the ability of solids to disintegrate under standardized conditions and can be expressed, for example, by the increase of the specific surface area per a unit of work consumed. A number of methods have been developed for determining grindability. The main methods are VTI, Bond, Zeisel and Hardgrove.

The Hardgrove method was designed in 1930 by Ralph M. Hardgrove as a method of determining the grindability of coal. This method uses a small amount of material with a specific granularity, which is ground in a grinding track by 8 grinding balls. The test ends after 60 revolutions of the mill. After milling, the material is sifted through a 0.075 mm sieve. Then, HGI (Hardgrove grinding index) is calculated and expressed in °H. The method was designed for grinding coal, but it later expanded to other materials as well [6].

Another method is the Zeisel method, which was invented in 1953 and is based on Hardgrove. It uses a similar apparatus but operates at 100 to 200 mill revolution instead of 60. The result is the amount of specific energy expressed in kWh<sup>-1</sup>, which must be spent in order to achieve a specific level surface area according to the Blaine permeability method. The grindability is then expressed in kJ·kg<sup>-1</sup>. [6]

The Bond method is the most frequently used one. In contrast with the two previous methods, it uses a ball mill with the diameter and length of 305 mm, which is filled with a specific number of grinding balls with different diameters. The material being ground must have grain size below 3.35 mm. The goal is to find the correct number of rotations to achieve a specific ratio of rejects (oversized) and fines (undersized) on 106 µm sieve. The result is expressed in kWh/t the values reach 6 – 9 for well grindable materials and over 20 for poorly grindable materials [7].

The last method is VTI (also known as RTI after Russian Thermal Energy Institute) [8]. This method is the simplest of all those described here. A porcelain laboratory ball mill with the capacity of 1.5 dm<sup>3</sup> and a porcelain grinding medium is used. The diameter of the grinding bodies is 25 mm and their total weight is 4 kg. The material being ground has a grain size between 1.25 and 3 mm. The weight of the sample is 500 g. Grinding takes 6 minutes, during which the apparatus performs 540 revolutions. In the end, the oversize remainder on the sieve 0.09 mm is measured. This amount is then substituted into the formula (1) to calculate the grindability index  $K_{VTI}$  of the material

$$K_{VTI} = 2 \left( \ln \frac{100}{Z_{0,09}} \right)^{\frac{2}{3}} \quad (1)$$

where  $Z_{0,09}$  is remainder on sieve 0,09 mm. According to the  $K_{VTI}$  index, the materials can be classified into the following groups:  $K_{VTI} > 1.8$  for the easily grindable  $0.8 \leq K_{VTI} \leq 1.8$  for the moderately grindable and  $K_{VTI} < 0.8$  for the poorly grindable [2].

All the above-mentioned methods have one common feature, namely the need for special equipment, which has no other use besides the given test. This was the motivation for the modification of the VTI method, to make use of a more common grinding device and also to modernize the method. Two major modifications were made. The first one was the use of a commonly used planetary ball mill and the second one was the attempt to employ laser granulometry instead of sieve analysis for evaluation.

## 2. Materials and methods

The first step was to analyze the raw materials. Three materials were used; recycled glass, Portland clinker from a local cement plant Hranice and granulated blast furnace slag. The chemical composition was determined by means of gravimetric analysis. Results of chemical analyses of the materials used are shown in Tables 1 to 3. The first table shows chemical composition of the recycled glass.

**Table 1.** Chemical composition of recycle soda-lime-silica glass.

Components	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Others
Content [%]	69.25	8.09	0.83	0.41	16.44	4.98

Results show a high content of amorphous SiO<sub>2</sub>. Based on this, an admixture of recycled glass could contribute to the mechanical properties, because of its pozzolanic activity [9]. Table 2, lists the chemical composition of the Portland clinker.

**Table 2.** The chemical composition of clinker.

Components	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Others
Content [%]	20.29	65.33	1.07	5.21	5.04	1.05	0.14	1.87

This chemical composition is typical for alite Portland clinker. The results of the chemical analysis of blast furnace slag are shown in Table 3.

**Table 3.** The chemical composition of granulated blast furnace slag.

Components	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Others
Content [%]	38.34	40.80	4.80	0.49	0.46	15.11

This material is currently used as a latently hydraulic admixture in cement production. Cement with an admixture of this material is according ČSN EN 197-1 identified by the suffix S. [10].

Grindability was also measured on mixtures of clinker and glass or blast furnace slag. These mixtures were prepared at a constant weight ratio of 20:80; i.e. 20 % replacement of clinker. This ratio was found successful in previous research.

All grindability tests were performed in a Fritsch planetary ball mill Pulverisette 6 in a bowl with the volume of 0.5 dm<sup>3</sup>. 25 grinding balls with 20 mm in diameter were used. The comminution of the material to be ground takes place primarily through the high-energy impact of the grinding balls. The grinding bowl, containing the grinding balls and the material to be ground, rotates around its own axis on the main disk whilst rotating rapidly in the opposite direction. Centrifugal force causes the ground sample material and the grinding balls to separate from the inner wall of the grinding bowl. The grinding balls then cross the bowl at high speed and further grind the sample material by impact against the opposite wall of the wall. Because the chosen mill is not typical for the VTI grindability test, it was necessary to optimize the grinding cycle. The optimization was performed on 150 g of clinker because it is a moderately grindable material. The initial granularity was the same as for the regular VTI method; within the range of 1.25 and 3 mm. A number of parameters were monitored. Sticking of the material was monitored visually. The movement of the grinding bodies was monitored acoustically. Also, heating of the grinding bowl was observed. The milling time was optimized for clinker. For this, the measured criterion was oversize residue on a 0.041 mm sieve which was set to 70 %. A Matest Air jet sieve was used to determine the oversize residue in all cases.

As written in the introduction, a modified VTI method was used. The main modification was in the grinding apparatus. Besides oversize on a 0.09 mm sieve, residues on 0.063, 0.041 and 0.02 mm were monitored also. Granularity was also determined by means of laser granulometry. For this a laser granulometer Mastersizer 2000 was used. Representations of the particle size of the individual tests were then compared to determine the substitutability of sieve analysis for the newer method while exploring options for the assessment of grindability of finer particles.

### 3. Results

Based on the aforementioned parameters, such as the movement of grinding bodies, their heating, sticking of the material to them and the walls of the grinding bowl and lastly oversize on a 0.041 sieve, the optimal grinding mode for the selected material was 2 minutes at 300 rpm. In this mode, the ground

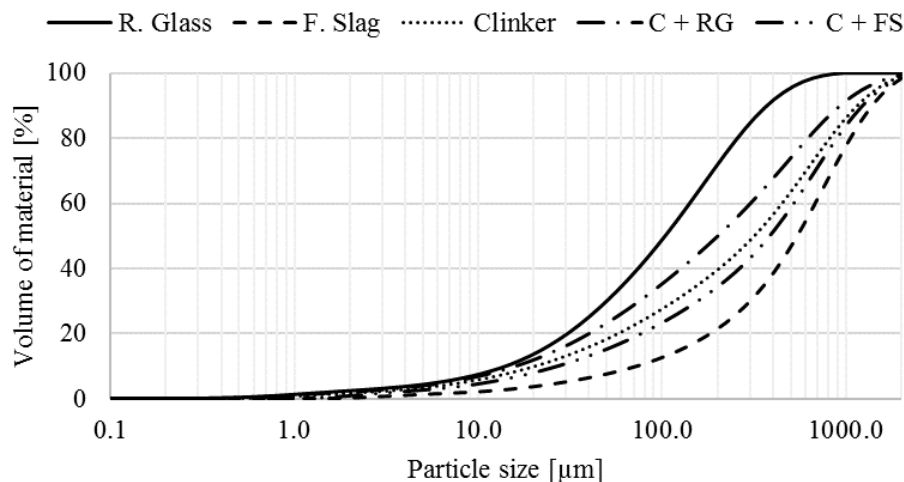
material did not stick to the grinding bowl or balls. The movement of the grinding bodies in the bowl was optimal. The temperature of the grinding bowl did not exceed 40°C.

Results of the sieve analysis after grinding performed by a vacuum sieve represented by oversize % are shown in Table 4.

**Table 4.** Sieve analysis of materials after grinding, oversize %.

Material	Sieve size [mm]			
	0.020	0.041	0.063	0.090
Clinker	80.7	65.53	54.81	43.02
F. Slag	91.02	82.53	75.72	63.73
R. Glass	79.92	49.52	31.18	12.06
C + RG	82.16	59.07	47.21	33.27
C + FS	84.7	69.22	59.5	47.56

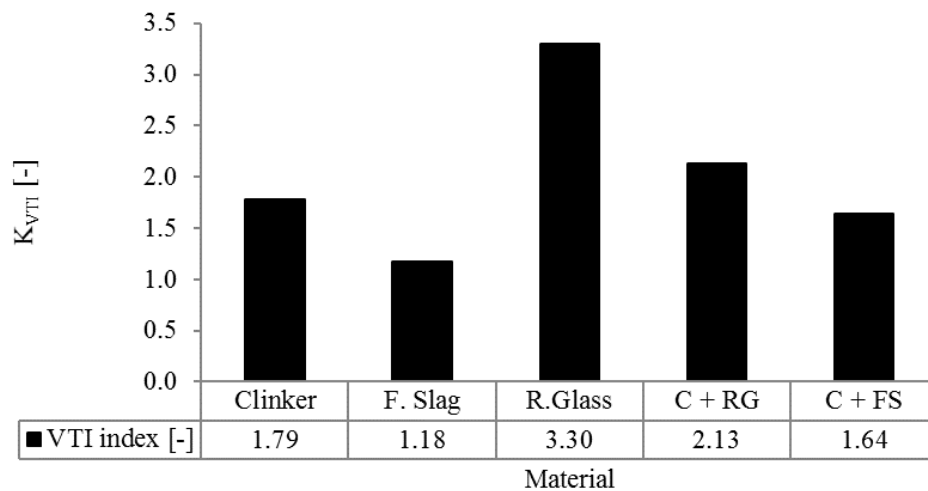
Results of laser granulometry, represented by an oversize distribution, is shown in the graph in Figure 1.



**Figure. 1.** Particle distribution of ground material obtained by laser granulometry.

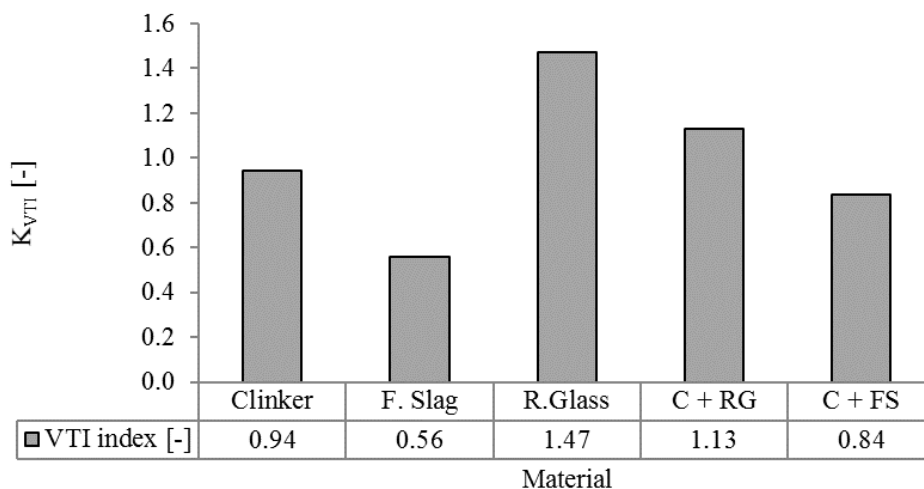
Grain size distribution curves describe the same trend as the sieve analysis, but in higher absolute numbers. This is caused by the method of measurement, since the sieve analysis may be considered less accurate in the case of this particle size.

Figures 2 to 6 summarize the results of the calculated grindability index  $K_{VTI}$  according to the equation (1). Figure 2 shows the value  $K_{VTI}$  calculated from oversize on a 0.09 mm sieve.



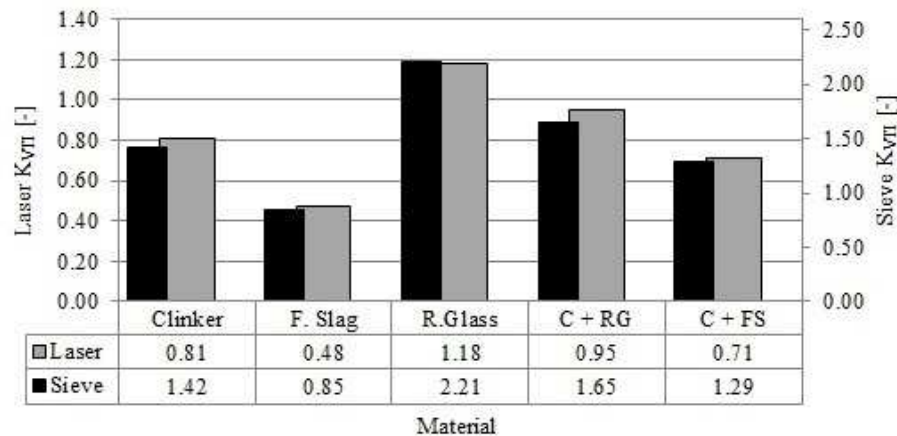
**Figure. 2.**  $K_{VTI}$  values calculated from oversize on sieve 0.09 mm.

Results show that blast furnace slag was harder to grind than other 2 materials. On the other hand, recycled glass has the biggest  $K_{VTI}$  index, i.e. has the best grindability. This is reflected also in mixtures, wherein the clinker-glass mixture is better grindable than the clinker-furnace slag mixture. Figure 3 shows the calculated results from laser granulometry for the same particle oversize.

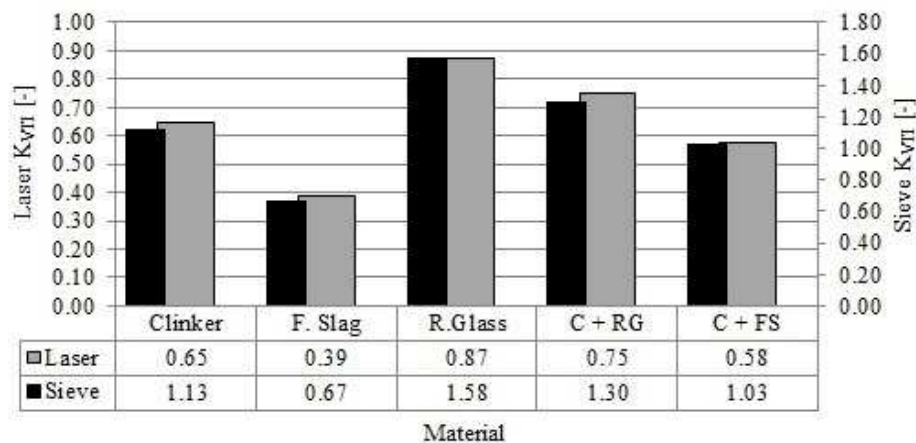


**Figure. 3.**  $K_{VTI}$  values calculated from laser granulometry for oversize 0.09 mm.

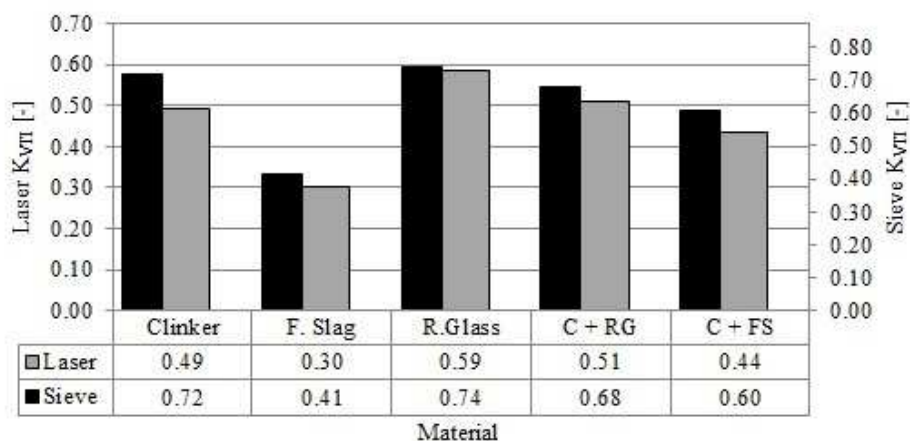
The values indicate that the  $K_{VTI}$  calculated this way is smaller in absolute values, but the trend is retained. The value reduction can be attributed to a different principle of measurement. Figures 4 to 6 show the results calculated for lower particle size and compare the values obtained by vacuum sieve analysis and by laser granulometry. Figure 4 shows the comparison for particles above 0.063 mm, Figure 5 for particles over 0.040 mm and Figure 6 for particles over 0.020 mm.



**Figure. 4.** Comparison of  $K_{VTI}$  calculated from sieve analysis and laser granulometry, 0.063 mm.



**Figure. 5.** Comparison of  $K_{VTI}$  calculated from sieve analysis and laser granulometry, 0.041 mm.



**Figure. 6.** Comparison of  $K_{VTI}$  calculated from sieve analysis and laser granulometry, 0.041 mm.

The results show that the trend remains the same for all particle sizes. However, we can observe a reduction in the grindability index when dealing with smaller particles. This results in a reduction of the differences between the values for each material. This trend is more significant in values calculated from the sieve analysis. For example, we can see that  $K_{VTI-0.02}$  for glass and clinker measured by the sieve



analysis is essentially the same, at 0.72 and 0.74. However,  $K_{VTI-0.02}$  values calculated from laser granulometry for these two materials are 0.49 and 0.59.

Values of  $K_{VTI}$  for clinker and blast furnace slag on all sieve sizes are compared to recycled glass in Table 5 to better display their relative ratio.

**Table 5.** Comparison of  $K_{VTI}$  ratio of clinker and furnace slag relative to recycled glass.

Method	Material	Sieve size [mm]			
		0.02	0.041	0.063	0.09
Sieve	Clinker	97 %	71 %	64 %	54 %
	F. Slag	56 %	42 %	38 %	36 %
Laser	Clinker	84 %	74 %	68 %	64 %
	F. Slag	52 %	44 %	40 %	38 %

An interesting effect can be observed. When evaluating the  $K_{VTI}$  index for finer particles, differences between materials become lower with each step.

#### 4. Discussion

Firstly, a chemical analysis of the materials was made. The chemical composition of the clinker can be regarded as normal for alite clinker commonly used in the production of Portland cement. The granulated blast furnace slag was also of standard composition and is widely used as an addition to blended Portland cement. The recycled glass contains a large amount of amorphous  $\text{SiO}_2$ , reaching values close to 70 %. The amount of alkali is similar to the theoretical values of soda-lime-silica glass. The content of alkali in the recycled glass does not cause problems if used in the form of very fine particles [11].

The optimal grinding mode was, based on various parameters, determined to be 2 minutes of grinding at 300 rpm. All grindability tests were made using this mode. Based on the values obtained by sieve analysis, shown in Table 4, we can state that recycled glass is more grindable than clinker or blast furnace slag since the oversize on a 0.09 mm sieve was only 12.06 %. For comparison, clinker had 43.02 % of oversize and blast furnace slag had even more at 63.73 %. The same order was observed in the results from laser granulometry, as seen in Figure 1, although there was a difference in values. The recycled glass had 53 % of volume over 0.09 mm, clinker around 72 % and blast furnace slag over 86 %.

A better comparison of grindability can be seen from the calculated values of the  $K_{VTI}$  index. The values for recycled glass are for both methods of determination of oversize content nearly double than those for clinker, or triple when compared to blast furnace slag. When comparing mixtures of materials, we can observe the anticipated results.  $K_{VTI}$  index for the mixture of recycled glass and clinker is about 20 % higher than for clinker alone. This is due to the synergistic effect of co-grinding of these materials [12]. On the other hand, the  $K_{VTI}$  index for the mixture of clinker and blast furnace slag is around 10 % lower than for clinker alone. This applies for both methods of determination of oversize content, sieve analysis, and laser granulometry.

When comparing the ratios of  $K_{VTI}$  indexes for clinker, recycled glass and blast furnace slag on smaller particles we can state that smaller particles are harder to disintegrate. This is observed in the shrinking gap between the values of indexes of the material, as seen in Table 5. For example,  $K_{VTI}$  calculated from sieve analysis for oversize 0.09 mm for clinker is only 54 % of the value of recycled glass. For oversize on a 0.02 mm sieve, clinker and glass have basically the same grindability index. This effect is less pronounced when oversize is determined by laser granulometry but is still noticeable. The ratio between blast furnace slag and glass is not affected by the measurement method, only by the size of particles. The differences are much smaller than for clinker/glass ratio.

Because the observed trends of values for laser granulometry and sieve analysis are similar, we can state that these two methods could be interchangeable, if correct a conversion rate is set. The indexes of  $K_{VTI}$  of the materials are only approximate since a planetary mill was used instead of a standard laboratory ball mill. These values could not be classified into groups according to the standard test and

serve only for mutual comparison. Therefore, it is necessary to perform a comparative test in accordance with the GOST 15489.1 standard, based on which a conversion relation can be drawn. However, when a constant grinding mode remains, the amount of energy delivered to the system is always the same and therefore the test is reproducible. Thus it is possible to consider the substitution of a specific mill by a more commonly used one.

## 5. Conclusion

Results presented in this paper show the possibility of modifying the VTI method. Firstly, the grinding apparatus was changed from a highly specialized one to one more commonly used. Secondly, the evaluation of oversize fraction was carried not only by means of sieve analysis but also by laser granulometry. It was found that the trends of the grindability index  $K_{VTI}$  remain the same, regardless of the method used. However, the absolute values are not comparable with the standardized method and it is necessary to establish an additional conversion relation. Nevertheless, these modifications allow the use of a more commonly used grinding apparatus and also to refine the evaluation of grinding of very fine particles.

## Acknowledgement

This work was financially supported by project number: 15-08755S “Study of effects of samples preparation on inorganic binders final properties” and project No. LO1408 “AdMaS UP - Advanced Materials, Structures and Technologies”, supported by Ministry of Education, Youth and Sports under the „National Sustainability Programme I

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