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To cite this article: D Sklenarova et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 385 012051

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Usability of alternative admixtures for the potential production of blended cements

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Abstract. This paper studies how pozzolan materials can be mechanically activated. For this, two major grinding technologies and different types of artificial pozzolans, such as red brick dust, granulated blastfurnace slag and sheet glass, were used. Observed properties were chemical and mineral composition, amorphousness, particle size and specific surface area. Pozzolan activity of selected materials was compared by evaluation of the reaction with lime using X-Ray diffraction (XRD) analysis and differential thermal analysis (DTA).

1. Introduction
Pozzolans are materials, which do not harden themselves, nor by the effect of the exciter, but because of their high amorphous siliceous or siliceous and aluminous content, it is capable to react with calcium ions to form similar hydration products (calcium silicate hydrates and calcium silicate aluminate hydrates) such as alite or belite.

The use of natural pozzolans, such as trass, tuffs, volcanic ash or pumices, is known from the Neolithic period [1]. Contrary to this, artificial pozzolans as an admixture with exceptional properties was used in the construction since Classical Antiquity [2]. It is known that the Roman Empire used both types of pozzolans. Natural ones such as those from city Pozzuoli located nearby volcano Mount Vesuvius, but they they purposefully created a binder with pozzolan properties by mixing crushed bricks with lime [3].

Recently, the frequently discussed topic is about the tendency to reduce CO₂ emissions from cement production. There are many options that directly reduce emissions. One of the options, how to reduce the emissions of CO₂, NOₓ, SOₓ and other substances is replacing a certain amount of cement with secondary raw materials with pozzolan properties such as microsilica or metakaolin, however, these materials are expensive today, so materials of similar properties with a lower purchase price are sought. Therefore, we cannot directly reduce emissions in cement production, but we can indirectly reduce them in relation to the unit quantity of resulting blended cement of the same or better properties than pure Portland cement. This has a significant impact on the ecology of cement production [4].

In this experiment, we had monitored whether the mechanical activation had occurred and the conditions during this process. One way to prove the effect of mechanical activation is to compare the grinding methods. The effort was to achieve the same specific surface area for both grinding methods and to monitor outputs of XRD and DTA analysis.

2. Materials and methods
Three materials were selected for testing - Red Brick Dust (RBD) made from grinded brick (Heluz 2012), Sheet Glass (SG) from the old window glass and Granulated Blastfurnace Slag (GBS) from power station Dětmarovice (2017). On each of them a chemical analysis and X-Ray diffraction (XRD)
analysis was performed. For research, two grinding methods were used – grinding in a vibratory disc mill and in a laboratory planetary mill. The specific surface area was measured by using a ZEB PC-Blaine Star. The milled samples were mixed with lime immediately after milling, and pozzolan activity was then monitored by using X-Ray diffraction (XRD) analysis and differential thermal analysis (DTA) after 1, 7 and 28 days.

To ensure grinding efficiency, all materials were first crushed to a maximum grain size 2 mm. Granulated Blastfurnace Slag did not have to be prepared in any way, because it was delivered already milled (specific surface area was 280 m²/kg). For measurement of specific surface area of samples, it is necessary to specify the density of the tested materials. Thus, the density of all materials was measured on the Micromeritics AccuPyc II 1340 helium pycnometer.

2.1. Method of grinding in a planetary mill
At first, the grinding was done in one-position planetary mill PULVERISETTE 6 (FRITSCH). For grinding was used 500 ml grinding bowl with 25 grinding balls. Rotational speed of main disk was 500 rpm. The actual grinding process was dry, so no liquid was added. Total batch of 200 g was ground to a specific surface area 500 m²/kg. From the beginning, 1–2 minutes grinding intervals were selected and then the grinding balls and bowl were cleaned. Later, the final specific surface area correction was done by using shorter, 30 seconds grinding intervals. Immediately after grinding, all samples were mixed with water and reactive CaO.

For this experiment, lime was specially prepared by burning CaCO₃ in a grade of purity analytical reagent. The temperature increase during burning process was 8 °C/min up to 1050 °C, where the temperature stayed for 4 hours. To determine the correct batch of CaO, it was assumed that the material was only reactive SiO₂, and so a gel of C₃S₂H₃ could form from a 100% of material. The ratio of CaO and materials was then determined from the molar masses.

\[
\begin{align*}
M(\text{Ca}) &= 40.08 \text{ g/mol} \\
M(\text{O}) &= 16.00 \text{ g/mol} \\
M(\text{Si}) &= 28.09 \text{ g/mol} \\
M(\text{CaO}) &= 40.08 + 16.00 = 56.08 \text{ g/mol} \\
M(\text{SiO}_2) &= 28.09 + 2(16.00) = 60.09 \text{ g/mol} \\
3 \cdot C &\rightarrow 3 \cdot M(\text{CaO}) = 3 \cdot 56.08 = 168.24 \text{ g/mol} \\
2 \cdot S &\rightarrow 2 \cdot M(\text{SiO}_2) = 2 \cdot 60.09 = 120.18 \text{ g/mol}
\end{align*}
\]

While maintaining a ratio of 168.24 g/mol of CaO to 120.18 g/mol of pozzolan (test materials), we provide sufficient amount of CaO to produce the ideal conditions for the C₃S₂H₃ gel formation. When we adjust this ratio, we come to a ratio of 1.4 g of lime per gram of test material.

2.2. Method of grinding in a vibratory disc mill
The second grinding method was done in vibratory disc mill RETSCH RS 200 with grinding bowl (size 100 ml). Each batch weighed 180 g and it was ground to a specific surface area 500 m²/kg. As with the planetary mill, it was necessary to do short grinding cycles (up to 1 minute) followed by cleaning the grinding bowl and tools, otherwise the grinding process became very inefficient. Rotational speed was 900 rpm. Next steps were the same as for grinding in the planetary mill and during the addition of CaO, the same calculated ratio was maintained (1.4 g : 1 g of test material).

2.3. Sample preparation for X-Ray diffraction (XRD) analysis and differential thermal analysis (DTA)
A batch for XRD and DTA analysis was 5 g (grinded material and CaO). The samples were ground for 3 minutes in a McCrone Micronizing Mill and subsequently dried at 55 °C. Samples of each material were taken after 1 day, 7 days and 28 days from mixing.
3. Results
The material characteristics of the samples were determined for the specification of input raw materials. In the first part, before grinding, chemical analysis and XRD analysis were done.

**Table 1. Chemical composition of the pozzolans.**

|                | Granulated Blastfurnace Slag (GBS) | Sheet Glass (SG) | Red Brick Dust (RBD) |
|----------------|-----------------------------------|------------------|----------------------|
| SiO$_2$ [%]    | 40.37                             | 71.74            | 70.38                |
| MgO [%]        | 2.01                              | 0.85             | 0.25                 |
| MnO [%]        | 1.21                              | 0.00             | 0.05                 |
| CaO [%]        | 47.09                             | 10.80            | 4.88                 |
| Al$_2$O$_3$ [%] | 7.85                              | 1.06             | 14.54                |
| TiO$_2$ [%]    | 0.41                              | 0.07             | 0.81                 |
| Fe$_2$O$_3$ [%]| 0.19                              | 0.03             | 5.17                 |
| Na$_2$O [%]    | 0.57                              | 15.02            | 0.90                 |
| K$_2$O [%]     | 0.61                              | 0.16             | 2.12                 |
| SO$_3$ [%]     | 0.27                              | 0.02             | 0.17                 |

From the chemical analysis, it is evident that the brick dust contains the highest amount of SiO$_2$. From the diffractogram was identified $\beta$-quartz, which coincided with the chemical composition of the material. The sheet glass had a high content of SiO$_2$ and Na$_2$O, which is typical for glass. Other oxides are present in very small amounts. XRD analysis of the glass was not performed because it is particularly amorphous material. The granulated slag compared with other observed materials contained the highest amount of CaO and the lowest amount of SiO$_2$.

3.1. Results of differential thermal analysis (DTA)
On the grounds that the chemical formula of C-S-H gels cannot be accurately determined, it was necessary to observe the total content of CaO in the samples. In figure 1 shows an example of a DTA analysis output, where two important reactions are marked.

- Reaction 1 - Decomposition of portlandite $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$
- Reaction 2 - Decomposition of carbonates $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
The next part was to express input and output substances from the reaction in molar amounts.

- Reaction 1 - Decomposition of portlandite $M(\text{Ca(OH)}_2) \rightarrow M(\text{CaO}) + M(\text{H}_2\text{O})$
- Reaction 2 - Decomposition of carbonates $M(\text{CaCO}_3) \rightarrow M(\text{CaO}) + M(\text{CO}_2)$

Calculation coefficients were also used to simplify the calculation. In Reaction 1, $\text{H}_2\text{O}$ is exited, which is reflected by weight loss of the sample.

$$\text{Calculation coefficient (Ca(OH)}_2) = \frac{M(\text{Ca(OH)}_2)}{M(\text{H}_2\text{O})} = \frac{74.0958}{18.0158} = 4.1128232$$

In Reaction 2, $\text{CO}_2$ is exited, which is reflected by weight loss of the sample.

$$\text{Calculation coefficient (CaCO}_3) = \frac{M(\text{CaCO}_3)}{M(\text{CO}_2)} = \frac{100.09}{44.01} = 2.2742558$$

For further evaluation, it was also necessary to determine the actual CaO content in the samples. Calculated content of portlandite and calcium carbonates was further recalculated to their net CaO content.

$$\text{CaO content in (Ca(OH)}_2) = \frac{M(\text{CaO})}{M(\text{Ca(OH)}_2)} = \frac{56.08}{74.0958} = 0.7568631$$

$$\text{CaO content in (CaCO}_3) = \frac{M(\text{CaO})}{M(\text{CaCO}_3)} = \frac{56.08}{100.09} = 0.5602957$$

Thus, if the sample weight loss was 10% in the temperature range 450 °C - 550 °C in reaction 1, it means that the sample contained $10\% \times 4.1128232 = 41.1\% \text{ Ca(OH)}_2$ and that contained $41.1\% \times 0.7568631 = 31.12844109\% \text{ CaO}$. It was similar for reaction 2. If the sample weight was 10% in the temperature range 650 °C - 900 °C, it means that the sample contained $10\% \times 2.2742558 = 22.7\% \text{ CaCO}_3$ and that contained $22.7\% \times 0.5602957 = 12.74255745\% \text{ CaO}$. The CaO content, which was calculated from both reactions together, indicates the total CaO content in the samples.

For the sake of clarity, the total CaO content calculated from both reactions obtained from DTA analysis of all samples (Granulated Blastfurnace Slag (GBS), Red Brick Dust (RBD) and Sheet Glass (SG)) is shown in figure 2 (grinded in the vibratory disc mill) and in figure 3 (grinded in the planetary mill).

![Figure 2](image-url) **Figure 2.** The calculated total content of CaO in the samples grinded in the vibratory disc mill after 1, 7 and 28 days of reaction.
3.2. Results of X-Ray diffraction (XRD) analysis
In this part, the size and shapes of the Ca(OH)$_2$ lines were mainly examined in X-Ray diffractograms.
As can be seen in the figure 4 and figure 5, the lowest intensity was reached by Granulated Blast furnace Slag grinded in the vibratory disc mill. Similarly, low intensity can be observed for Sheet Glass grinded in the planetary mill. On the contrary, Red Brick Dust grinded in the planetary mill reached very high intensity.

4. Discussion of results and conclusion

This paper deals with mechanical activation of pozzolans. The main result is the evaluation of the pozzolan activity of Sheet Glass, Granulated Slag and Brick Dust by DTA analysis. The amount of CaO in the samples mixed with lime in a given ratio was subsequently determined for different time intervals. A chemical analysis was performed and actual CaO content in the samples was found.

The highest actual CaO content was measured in samples of Granulated Slag (47.09%), which also had the largest loss of CaO during the measurement, which meant it had high pozzolanic activity. Mechanical activation due to grinding methods could also occur in the slag because a greater decrease in CaO on the samples grinded in the planetary mill was observed on the same specific surface (500 m²/kg).

The Sheet Glass showed very interesting results. The loss of CaO was very variable depending on used grinding technology. The glass grinded in the vibratory disc mill had a significantly higher CaO content and unchanged consistency after 28 days while the glass grinded in the planetary mill had after 28 lower CaO content and hard cracked structure. This pozzolan activity was caused by the high amount of SiO₂ and method of grinding in planetary mill, which apparently allowed to reach the limit of the plastic fracture, which means that we can consider this as a mechanical activation [5]. Recycled glass as an admixture for the production of blended cements can be a suitable alternative. Pozzolanic activity increases for high specific surface area and the high fineness of grinding ensures that the concrete does not degrade due to the alkali–silica reaction [6].

From all of the examined materials the losses of CaO were lowest in a Brick Dust sample with approximately 3% loss after 28 days of reaction. However, the total CaO content was very low and it is not possible to assume a pozzolanic reaction for this sample. By the experiment we have confirmed that the sample did not harden after 28 days of reaction.

In conclusion, it can be said that Granulated Slag and Sheet Glass can be mechanically activated, and they indicate pozzolan properties. So, it is possible to use such materials in the production of blended cements as an alternative admixture. For Brick Dust no such properties were observed.

5. Acknowledgements

This work was financially supported by project number: GA17-24954S “The Conditions of Thermodynamic Stability and Transformation of AFt Phases” 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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