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Research of siliceous fly ash after denitrification utilisation in ternary binders

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Abstract. The requirement to reduce the nitrogen oxide emissions in the production of electricity and heat by combustion of mainly brown coal leads to the installation of NO_x reduction technologies. The presented paper focuses on a partial replacement of Portland cement with siliceous fly ash after denitrification by a selective non-catalytic reduction method (SNCR) where urgent urea or ammonia water solution is injected into the combustion chamber. As the third component of the ternary binder the limestone and/or recycled concrete powder was used. The activity index of compressive strengths and the workability of mortars were tested in accordance with EN 196-1.

1. Introduction

Production of Portland cement requires a great deal of material to be extracted from nature. Subsequent crushing, homogenization, drying of cement-based raw material and excavation of the raw material itself is a major environmental burden. During production of one ton of cement, nearly one ton of CO_2 is produced too, as well. For this reason, modern concrete technology of concrete focuses on the possibility of lowering cement content in the concrete by partially replacing it. Cement can be partially replaced by one or more components. This article is focused on ternary binders, where 25 % of the cement weight is partly replaced by two components. These ternary binders are a promising way of concrete technology [1-4]. For experiments in this paper fly ash from the power plant using SNCR method and limestone or recycled concrete powder were used. An optimum composition of ternary binder can modify hydration reaction in a positive way and it can bring a synergic effect. The synergic effect of all three components brings about to obtain better properties such as higher early strengths in comparison with binary binders as well as better durability [1-2,4,6].

Fly ash, in general, has several positive benefits in its use for the production of the concrete mixture. Especially, there is a positive impact on the rheology of cement paste due to its suitable grain morphology and also reduction of the hydration heat development. However, in 2016 legislation regulating the limits of NO_x came into force. For this reason, power plants and heating plants are taking steps towards new technologies that allow us to reduce the amount of nitrogen oxides in the flue gas. One of the technologies is selective non-catalytic reduction method (SNCR). SNCR denitrification technology consists in spraying the reduction solution into the flue gas stream in the 850 – 1100 °C temperatures. The effectiveness of this method also depends on a number of other things, though the chemical, physical and mechanical properties of the collected fly ash are changing. Such fly ash contains more compounds of ammonia than the usual one and its morphological structure is damaged by the heat shock when the reducing agent is injected.

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2. Materials and experimental procedure

Some of the used fly ash properties after SNCR method are shown in table 1. To prepare the mortars, CEM I 42.5 R from Cement Hranice company was used. The composition of mortars is shown in table 2. Portion of the cement weight (25%) was replaced by fly ash with addition of limestone or recycled concrete powder. Sand normalized according to Czech standard ČSN EN 196 was used. Mortars were mixed in a laboratory mixer in accordance with EN 196-1. The workability was measured with a truncated cone, low base diameter 100 mm, upper base diameter 60 mm, height 60 mm. The cone flow was measured on a jolting table after 15 jolts in two perpendicular directions. Prepared mortars were put into molds (40 × 40 × 160 mm) and they were compacted. At the age of 24 hours, the specimens were demolded and 2 of them were tested for 24 hours strength. Other specimens were stored in water (with 20 ± 3 °C) until testing at the ages of 7 and 28 days. Every time the ternary mortars were made comparative, cement-plain specimens in accordance to EN 196-1 were also prepared.

Table 1. Some properties of fly ash.

	Date of withdrawal	pH ČSN ISO 10523 ČSN EN 12457-4	Ammonnia [NH_3] ČSN EN 12457-4 ČSN ISO 7150-1 [mg/kg]
Fly ash A	April 6, 2017	11.94	11.6
Fly ash B	January 29, 2018	12.08	19.8
Fly ash C	March 14, 2018	12.14	22.8

Table 2. Composition of mortars [kg/m^3].

Sign	0	6.5	12.5	18.7	25	CEM
CEM I 42.5 R	338	338	338	338	338	450
Fly ash	0	28	56	84	112.5	0
Recycled concrete powder P450 (or limestone)	112.5	84	56	28	0	0
Water	225	225	225	225	225	225
Normalized sand PG 1	450	450	450	450	450	450
Normalized sand PG 2	450	450	450	450	450	450
Normalized sand PG 3	450	450	450	450	450	450

2.1. Grain morphology of fly ash

The impact of SNCR method on fly ash was analyzed using electron scanning microscopy. A specimen of the fly ash which has been sprayed with a reducing agent and so-called pure specimen has been studied. However, when comparing fly ash after SCNR and without this method under a microscope, no significant difference in the fly ash structure was apparent (as it can be seen in figure 1 and figure 2). This is probably due to the low content of ammonia in fly ash. During mixing the fly ash after SCNR with cement and water, no release of ammonia into the air was observed. The power plant need to supply reducing agent in larger quantities for meeting the nitrogen oxide discharge limit is unlikely.

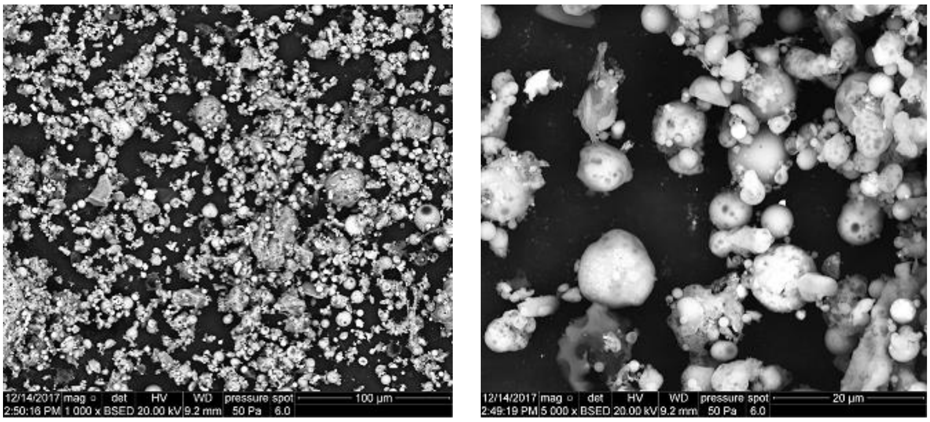

Figure 1. Grains of fly ash without SNCR method (magnified 1000x and 5000x).

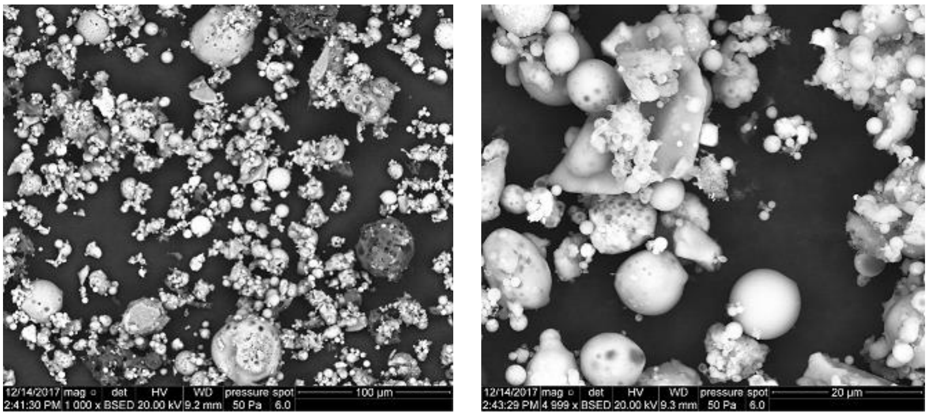

Figure 2. Grains of fly ash after SNCR method (magnified 1000× and 5000×).

3. Results and discussion

The presented results deal with the compressive strengths as well as workability of mortars with cement, fly ash after denitrification by the SNCR method in combination always with one more supplementary material – limestone or recycled concrete powder P450. Recycled concrete powder is made from concrete railway sleeper and contains 7.8 % of $CaCO_3$ and 18.8 mgCaO/g. Content of CaO includes $CaCO_3$ also.

3.1. Fly ash and limestone

At the age of 24 hours the highest compressive strengths are recorded for mixture with 25 % of fly ash after SNCR. The interesting thing about results are that there is not any significant synergy between fly ash and limestone at the age of 24 hours. Even at 7 days and 28 days the best strengths were recorded for ternary binder. Comparative cement mortar has the highest strengths – all activity indexes are lower than 100 % as we can see from figure 3.

The workability in figure 4 of each mixture improves with decreasing the proportion of fly ash in place of limestone. This is probably related to the higher absorptivity of water of the fly ash. Such as the fly ash after SNCR method, even the recycled concrete powder is another reason for worse workability.

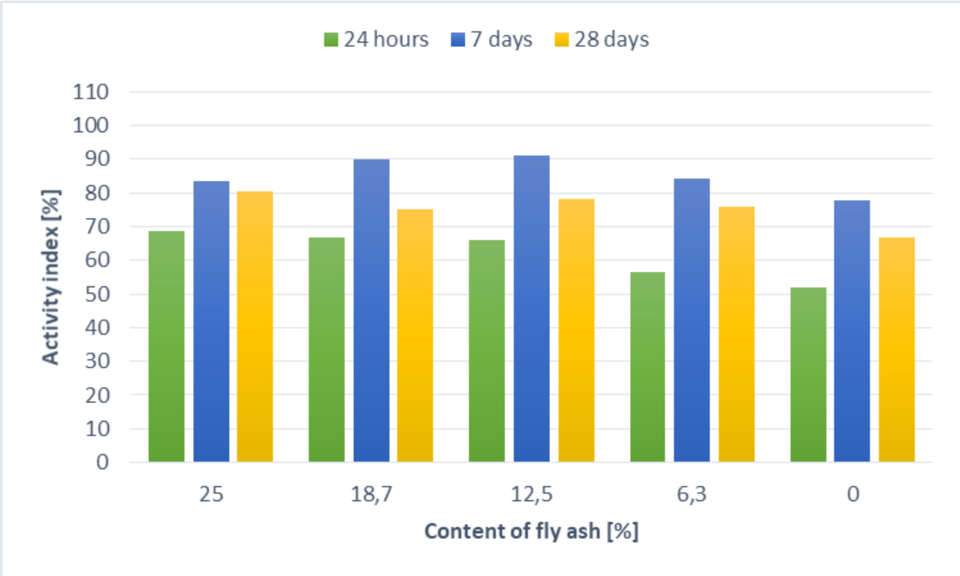

Figure 3. Activity index of compressive strength, 25 % of fly ash, and limestone.

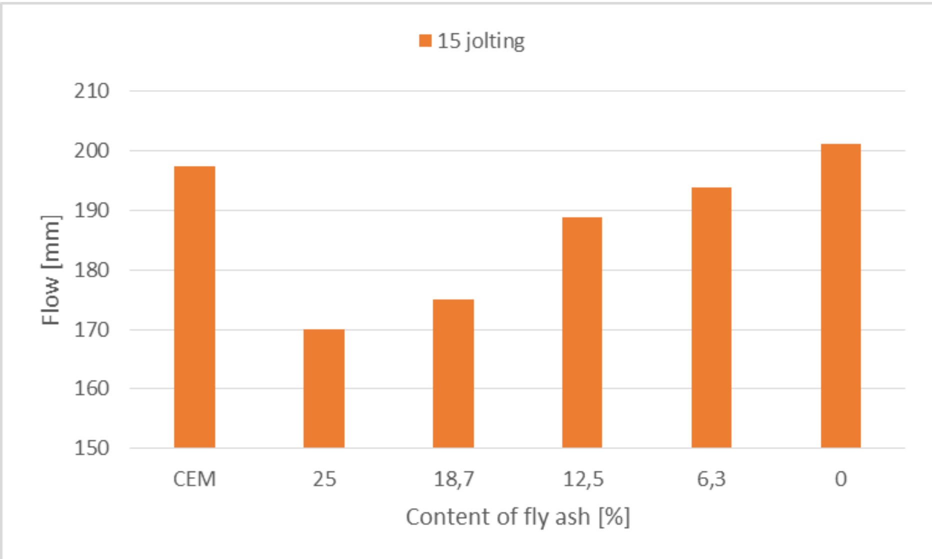

Figure 4. Workability of mortars, 25 % of fly ash, and limestone.

3.2. Fly ash and recycled concrete powder

For the combination of cement, fly ash and concrete powder the strong synergy at the age of 24 hours for the mortar with 6.3 % of fly ash can be seen in figure 5. At the age of 28 days the activity index is the highest for mortar with 25 % of fly ash. Comparative cement mortar has the highest strengths as well as mortars with limestone.

The workability in figure 6 is getting better with increasing the proportion of the recycled concrete powder. This fact, confirm high fly ash absorption of water. All workability considered, better workability for mortars with limestone was found. This is because finely ground limestone has a much lower absorption of water compared to the recycled concrete powder. Next research may focuses to use of plasticizer. This can improve the workability of mortars with fly ash after SNCR and recycled concrete powder.

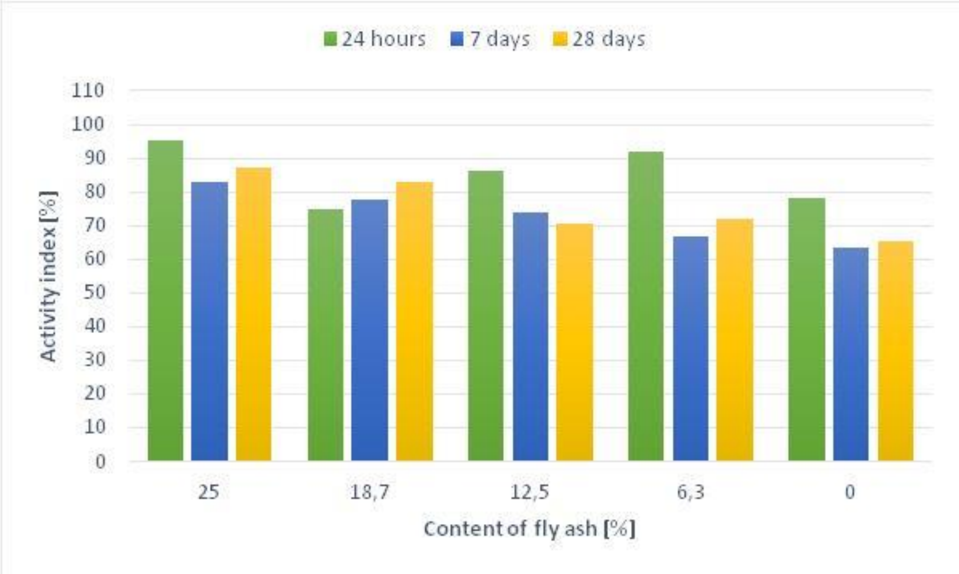

Figure 5. Activity index of compressive strength, 25 % of fly ash and recycled concrete powder P 450.

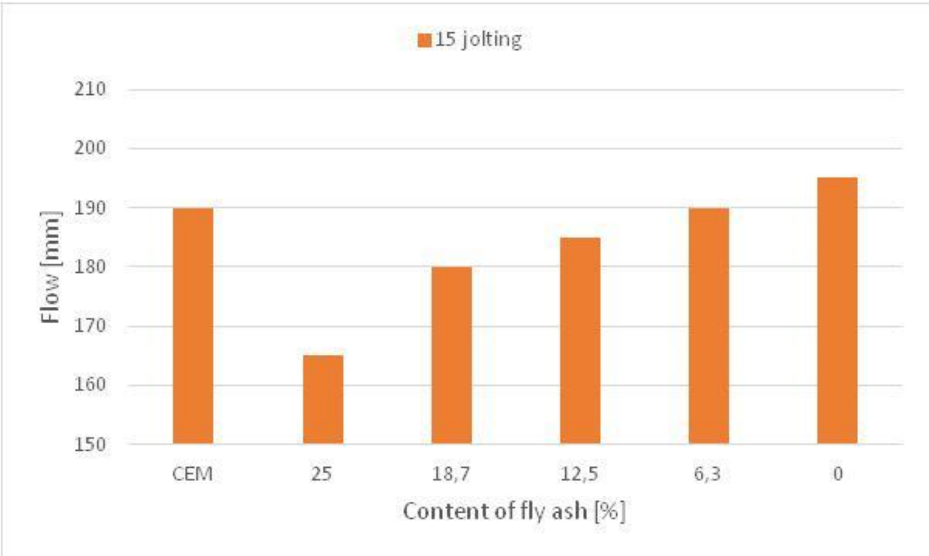

Figure 6. Workability of mortars, 25 % of fly ash, and recycled concrete powder P 450.

4. Conclusions

The presented results show the use of fly ash after SNCR method, limestone and recycled concrete powder in ternary binders. Fly ashes from a power plant are supplementary materials that are used successfully in concrete to improve the rheology of cement paste and to reduce hydration heat while reducing the total amount of cement in concrete. In conjunction, with one more supplement the binder is called ternary. Initial strengths and durability of ternary binders are typically better than of those with binary binders. However, the SNCR denitrification method can affect the fly ash but it is not know how. Fly ash, which was used, changes the properties of mortars. Especially workability as we can see above. This change leads to the worse rheology of cement paste. At the age of 28 days the activity index was similar for both types of mixtures.

Further research should focus on influencing the granulometry and other chemical and physical properties as on binary and ternary binders. Also, there should be research with other types of supplements.

It is above all the fact that fly ash properties are changing due to the changes in legislation and there is not enough information about how such fly ash will react in the cement paste. The same applies for binary and ternary binders.

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