Possibilities of ammonium ions fixation into mixed binders

J Hajzler¹, R Novotny¹, T Opravil¹ and P Ptacek¹
¹Brno University of Technology, Faculty of Chemistry, Purkyňova 464/118, Brno Cz-612 00, Czech Republic
E-mail: xchajzlerj@fch.vutbr.cz

Abstract. The purpose of this study is to analyze the usability of ammonium ions fixation in mixed binders with the addition of high temperature fly ash. The experiment used high-temperature fly ash from operations in which the secondary flue gas denitrification methods have been implemented, specifically by the method of the selective non-catalytic reduction, known as DeNOx. The fixation of ammonium ions was performed by the addition of sodium hexanitrocobaltate(III). The study examines the influence of addition of cobalt(III) complex compound on the release of ammonia into the environment during the mixing the mixed binder. The released ammonia was quantitatively captured into the acid and subsequently titrated. The effect of cobalt(III) complex compound on the rate of hydration and mechanical properties of the mixed binders was also studied. The influence on the environment in terms of leachability was observed.

1. Introduction
Combustion of coal or other materials in thermal power plants generates, in addition to solids parts, gaseous substances, including carbon oxides, sulphur and nitrogen oxides. Nitrogen oxides (referred to as NOₓ) are formed by the oxidation of nitrogen in fuels with air oxygen and are counted among the most dangerous pollutants. NOₓ contained in flue gases consists of NO (90%) and NO₂ (5%). They both are formed during combustion. NO (90–95%), which is initially formed colourless, odourless and then is transformed into a reddish-brown, acrid smelling NO₂. The residual nitrogen oxides are represented to a small extent (5%) and are often generated by the interaction of NO with NO₂ [1, 2, 3].

Emissions are air pollutants and therefore emission limits are set (ELV–emission limit values). There are ELVs to protect human health against the negative effects of NOₓ. The following table 1 states the NOₓ emission limits in mg/Nm³ for each category of combustion equipment accepted by the European Commission in 2017. These limits will come into force in the Member States at the turn of 2021/2022 [4].
Table 1. BAT-associated emission levels (BAT-AELs) for NOx emission to air from combustion of coal and/or lignite [4].

| Combustion plant total rated thermal input (MW) | BAT-AEL (mg/Nm$^3$) Yearly average |
|-----------------------------------------------|------------------------------------|
|                                               | New plant                          |
| < 100                                         | 100–150                            |
| 100–300                                       | 50–100                             |
| ≥ 300                                         | 50–85                              |
|                                               | Existing plant                     |
|                                               | 100–270                            |
|                                               | 100–180                            |
|                                               | 85–150                             |

To achieve these emission values, it is necessary to use the best available techniques (BAT). These techniques may be divided into two large groups. Techniques based on suppression of forming NOx are called primary measures and secondary techniques, which consist of elimination of the formed NOx. Secondary techniques contain selective reduction, namely selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) [5].

The SNCR method passes without the presence of a catalyst at higher temperatures of 950–1100°C depending on the reducing agent used. The removal efficiency of the method is usually around 50%. The SCR method takes place in the presence of the catalyst at temperatures of 170–510°C depending on the catalyst used. SCR efficiency is up to 90%. Ammonia water, urea and cyanuric acid are used as reducing agents for selective measures [6, 7].

Both methods (SCR and SNCR) are effective and chemically well-researched. Due to the secondary measures, in the flue gas is NOx reduces to 30 mg/m$^3$, it fulfils the strictest ELV [2, 8].

High-temperature fly ash is used as an admixture for concrete according to ČSN EN 206-1. Addition of the fly ash brings a number of benefits. The ash can optimize the grain curve, improves processability, increases the resistance of concrete in a chemically aggressive environment, reduces reversible contraction of concrete, etc. Secondary raw material partly substitutes cement, it reduces primary raw material consumption and reduces environmental impacts from the point of view of the production of greenhouse gases in cement production [9].

Another way to reduce the environmental impact of Portland cement production is the use of cement kiln by-pass dust (CKD). By-pass cement kiln dust is a fine-grained alkaline particulate material similar in appearance to Portland cement collected in the air-pollution control devices during the production of cement clinker. This material contains high concentrations of heavy metals and therefore should be disposed as a hazardous waste. Its chemical composition is not suitable for returning back into feedstock and, therefore, it has to be discharged. Nevertheless, the economic pressure caused by CKD disposal tends to its re-addition to the final cement product. Addition of CKD is about 3 wt. % into cement [10, 11, 12].

There are differences in chemical and mineralogical composition between the classic high-temperature fly ash and fluidized fly ash. Fluidized fly ash contains up to 20 wt. % SO$_3$, up to 15 wt. % CaO and an annealing loss up to 15 wt. %. For these reasons this fly ash cannot be evaluated according to ČSN EN 450, because it does not fulfil most of the prescribed technical criteria and cannot be used for the production of concrete according to ČSN EN 206-1 [9, 13].

After introduction of the SNCR process, high-temperature fly ash contains ammonium ions most often in the form of ammonium sulphate and ammonium hydrogen sulphate. The ammonia content is about 40 ppm (40 mg in 1 kg fly ash), while reducing NOx below 200 m/Nm$^3$. The pH increases by mixing the mixture of fly ash and cement with water. Ammonia is released very easily and quickly in an alkaline environment. High concentration of ammonia in the air has a negative impact on human health and industrial equipment. The release of ammonia is the reason why this fly ash is not used for the production of concrete [14, 15].

There are developing methods of ammonium ions elimination in mixtures containing by-products. These by-products are from the process of NOx conversion to nitrogen and water. One of these methods is elimination using tannin, which builds an ammonium ion into its structure. An insoluble ammonium...
salt is formed and ammonia is no longer released into the environment. Another method is found on the reaction of ammonium ions with sodium hexanitrocobaltate, when a conversion happens and an insoluble stable compound is formed [5, 7, 16].

In this article was researched the possibility of fixing ammonium ions in mixed binders where high-temperature fly ash was used after the DeNO\textsubscript{x} process. Elimination was performed using sodium hexanitrocobaltate added as an aqueous solution.

2. Experimental

2.1. Methods

The manual spectrometric method ČSN ISO 7150-1 was used to determine the ammonium ions in the tested fly ash [17]. The possibility of elimination was performed on the principle of capturing of released ammonia into hydrochloric acid. An airtight container was filled by the fly ash and cement. Subsequently, it was rinsed with nitrogen and the outlet from the container was led into hydrochloric acid. The water with dissolved complex was added into the loose mixture. The experiment lasted for one hour. The acid was subsequently titrated. Mechanical properties, compressive strength and flexural strength were measured on the complex strength test of building materials equipment DESTTEST 3310 (Betonsystem). Flexural strength and compressive strength were measured on each test specimen. The size of the individual prisms was 40 × 40 × 160 mm. The testing specimens were kept in a humid environment. Mechanical tests were performed after 1, 2, 4, 7, and 28 days. The effect of cobalt complex compound on the hydration process was studied on an isothermal calorimeter (TAM Air). Aqueous extracts were prepared from mixtures after mechanical tests after 1, 2, 4, 7 and 28 days. Ten times larger volume of the distilled water was added to the weighted amount. Samples were placed in a head-heel shaker for 24 hours. Thereafter, measurements were made and cobalt values were determined. The method was performed by means of inductively coupled plasma emission spectroscopy (ICP – OES). In this work the ICP–OES method was performed using the ULITMA 2 (HORIBA Scientific).

2.2. Materials

In the experiment, high-temperature fly ash was used after the SNCR process from the Počerady coal-fired power plant. The main crystalline phases are formed by mullite and quartz. Furthermore, hematite, magnetite and anatase are represented. The residue is an amorphous. The phase composition of CKD was determined with X-ray diffraction (XRD). CKD mainly consisted of KCl, K\textsubscript{2}SO\textsubscript{4}, CaO, K\textsubscript{2}O and C\textsubscript{2}S. Cement 42.5 R (plant Mokrá, CZ) was also used. Its specific surface area was 2.438 m\textsuperscript{2}/g measured at high-speed surface area analyzer NOVA 2200e (Quantachrome INSTRUMENTS), and the chemical composition is given in table 2. For the production of testing specimen was used coarse, medium and fine. Sodium hexanitrocobaltate has been prepared at the Faculty of Chemistry [12, 18].

| Component | SiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | Fe\textsubscript{2}O\textsubscript{3} | CaO | MgO | SO\textsubscript{3} | Na\textsubscript{2}O | K\textsubscript{2}O |
|-----------|-----------------|-----------------|-----------------|-----|-----|--------|--------|--------|
| Cement    | 19.1            | 4.2             | 3.5             | 63.4| 1.0 | 2.6    | 0.1    | 0.9    |

2.3. Sample composition

Five mixtures were prepared. The composition of the individual mixtures is shown in table 3. Individual mixtures differ only in the addition of sodium hexanitrocobaltate to water. The water to binder (w/b) ratio was selected to be 0.5. The water coefficient is the ratio of water to binder. Because the cement is replaced by fly ash, the water coefficient is calculated to the sum of the added fly ash and cement. The ratio of coarse, medium and fine sand was 1:1:1. The ratio of sand to binder was 3:1.
Table 3. The composition of mixtures for mechanical properties.

| Sample | Fly ash [g] | Cement [g] | Sand [g] F/M/C | Water [g] | Sodium hexanitrocobaltate(III) [mg] |
|--------|-------------|------------|----------------|-----------|------------------------------------|
| A      | 225         | 225        | 450/450/450    | 225       | 0                                  |
| B      | 225         | 225        | 450/450/450    | 225       | 37.5                               |
| C      | 225         | 225        | 450/450/450    | 225       | 75                                 |
| D      | 225         | 225        | 450/450/450    | 225       | 150                                |
| E      | 225         | 225        | 450/450/450    | 225       | 500                                |

The composition of the individual mixtures in which was researched the influence of the addition of sodium hexanitrocobaltate on releasing of gaseous ammonia is shown in table 4. The mixture was formed from fly ash and cement in a ratio of 1:1. The cobalt complex was dissolved in water and subsequently added to the mixture. The water to binder ratio was 0.21. The low coefficient was selected to humidification the mixture and subsequently to initiate hydration and to produce alkaline pH. Gaseous ammonia was then released. If the water coefficient is higher, the gaseous ammonia could be captured into the surplus of water in the mix.

Table 4. The composition of mixtures for titration.

| Sample | Fly ash [g] | Cement [g] | Water [g] | Sodium hexanitrocobaltate(III) [mg] |
|--------|-------------|------------|-----------|------------------------------------|
| F      | 600         | 600        | 252       | 0                                  |
| G      | 600         | 600        | 252       | 100                                |
| H      | 600         | 600        | 252       | 200                                |
| I      | 600         | 600        | 252       | 400                                |
| J      | 600         | 600        | 252       | 1 333                              |

3. Result and discussion

By manual spectrometric method, it was determined that high temperature fly ash after the SNCR process from the Počerady coal-fired power plant contained 36.11 ±0.42 ppm of ammonia. The ammonia released by mixing the particular mixtures, was quantitatively captured into the acid and subsequently titrated. From the results of consumptions of individual titrations does not ensue the dependence. Differences in individual consumptions are within the error rate of the method. The time dependence on flexural and compressive strengths on the formed mixtures measured on testing beams after 1, 2, 4, 7 and 28 days is shown in figure 1 and figure 2.

Mixture B with a cobalt complex content of 37.5 mg has the highest flexural strength values. The maximum value was 4.67 MPa. With the increasing content of the added complex, the strengths are not significantly influenced. The most significant decrease was observed in the 28-day strength of the mixture D. Overall, it is possible to state that the differences among the measurements of the individual mixtures are due to statistical deviation.

A similar trend can be seen in figure 2. The highest strength values were observed again in mixture B, where the highest value reached 23.86 MPa. The mechanical resistance regularly increases with increasing time in all mixtures. There was no significant decrease in any value compared to the values without content of sodium hexanitrocobaltate.

In general, it is possible to state that the flexural and compressive strengths increase with increasing time both in the mixture without the addition of sodium hexanitrocobaltate and with its gradual addition.
Therefore, it was concluded that the addition of sodium hexanitrocobaltate in the selected concentrations to the mixing water does not influence the resultant mechanical properties of the tested specimen.
The calorimetry curve, shown in figure 3, shows the hydration process of the prepared mixtures. The standard hydration process of cement can be observed. Samples were composed of fly ash and cement in a ratio of 1:1. The hydration process is the same as hydration process of reference without the addition of other compounds. High-temperature fly ash has only a dilution effect here because the heat flow acquires half the value [19]. A powder complex was subsequently added to the dry mixture. From the calorimetry curves is evident that the hydration rate is not influenced by the addition of cobalt complex.

![Figure 3. Calorimetry curve.](image)

Aqueous extracts were analysed by the ICP–OES method. The devices detection limit is 35 mg·l\(^{-1}\). All analysed samples are below the devices detection limit. Cobalt is not leached into water from the cobalt complex added to the mixing water.

4. Conclusion
This work was focused on the possibilities of fixation of ammonium ions in mixed binders. An ammonium ion elimination method was tested by using sodium hexanitrocobaltate, which was added to the mixing water. Testing specimens were formed from mixtures to testing of mechanical properties and the samples were subjected to measurements on the isothermal calorimeter and their aqueous extracts were subjected to measurements on ICP–OES to determining the cobalt.

From the measured results of the mechanical properties of the formed specimens ensue that the addition of sodium hexanitrocobaltate does not influence the resultant strengths. Differences in flexural and compressive strengths among the individual mixtures are within the statistical deviation. Calorimetry curves also confirmed that the addition of cobalt compound does not influence the hydration process. Added cobalt compound is not released from the testing specimens, which is proved by leachability measurements. Mixing the mixtures and the capturing of ammonia into the acid didn’t confirm the assumption that the amount of released ammonia decrease with increasing addition of the complex. This is probably due to the insufficient addition of the complex. The mixture contained not only ammonium ions from high-temperature fly ash, but also potassium ions from the addition of bypass dust in cement.
Acknowledgement
This work was supported by specific research FCH-S-18-5194 and with the financial support by the project: GA19-16646S “The elimination of the negative impact of zinc in Portland cement by accelerating concrete admixtures”, with financial support from the Czech Science Foundation.

References
[1] Gómez-García M A, Pitchon V and Kienemm anna A 2005 Pollution by nitrogen oxides: an approach to NOx abatement by using sorbing catalytic materials Environment International. Elsevier Ltd. 31(3) pp 445–467
[2] Gohlke O 2010 A new process for NOx reduction in combustion systems for the generation of energy from waste Waste Management 30(7) pp 1348–1354
[3] Shi-long F, Song Q and Yao Q 2015 Study on the catalysis of CaCO3 in the SNCR deNOx process for cement kilns Chemical Engineering Journal 262 pp 9–17
[4] Prováděcí rozhodnutí komise (EU) 2017/1442: kterým se stanoví závěry o nejlepších dostupných technikách (BAT) podle směrnice Evropského parlamentu a Rady 2010/75/EU pro velká spalovací zařízení 2017 (Brusel) L212
[5] Hajzler J 2016 Možnosti eliminace čpavkového skluzu v technologických vodách elektráren (Brno)
[6] Van Caneghem J, De Greef J, Block Ch and Vandecasteele C 2016 NOx reduction in waste incinerators by selective catalytic reduction (SCR) instead of selective non catalytic reduction (SNCR) compared from a life cycle perspective: a case study Journal of Cleaner Production Elsevier Ltd 112(5) pp 4452–4460
[7] Hajzler J, Opravil T, Pořízka J and Ptáček P 2018 Possibilities of elimination of ammonia slip from technological water in power plants IOP Conference Series: Materials Science and Engineering. IOP Publishing 379 pp 1–7
[8] De Greef J, Villani K, Goethals J, Van Belle H, Van Caneghem J and Vandecasteele C 2013 Optimising energy recovery and use of chemicals, resources and materials in modern waste-to-energy plants Waste Management. Elsevier Ltd 33(11) pp 2416–2424
[9] Popílek a jeho použití do betonu: Vyhovující nové betonářské normě ČSN EN 206-1 (Svaz výrobců cementu ČR) p 4
[10] Kalina L, Bílek V, Kiripolský T, Novotný R and Másilko J 2018 Cement Kiln By-Pass Dust: An Effective Alkaline Activator for Pozzolanic Materials Materials 11(9)
[11] Eckert J O and Guo Q 1998 Heavy metals in cement and cement kiln dust from kilns co-fired with hazardous waste-derived fuel: application of EPA leaching and acid-digestion procedures Journal of Hazardous Materials 59(1) pp 55–93
[12] Abdel-Ghani N T, El-Sayed H A and El-Habak A A 2018 Utilization of by-pass cement kiln dust and air-cooled blast-furnace steel slag in the production of some "green" cement products HBRC Journal 14(3) pp 408–414
[13] ČSN EN 450-1:2013 Popílek do betonu: Část 1: Definice, specifikace a kritéria shody (Praha)
[14] Beranová D, Opravil T, Ptáček P and Snop R 2018 Release of ammonia from conventional power plant fly ash after the introduction of SNCR process IOP Conference Series: Materials Science and Engineering 379 p 6
[15] Elektrárna Počerady 2019 (Praha: Skupina ČEZ: Výroba elektřiny)
[16] A method of stabilizing residual ammonia in a mixture containing energy by-products using tannin 2017
[17] ČSN ISO 7150-1:1994 Jakost vod stanovení amonních iontů: Manuální spektrometrická metoda (Praha)
[18] Bílek V, Pařízek L and Kalina L 2015 Effect of the by-pass cement-kiln dust and fluidized-bed-combustion fly ash on the properties of fine-grained slag-based composited Materiali In Tehnologije 49(4) pp 549–552
[19] Šiler P, Kolářová I, Novotný R, Másilko J, Pořízka J, Bednárek J and Švec J 2018 Application
of isothermal and isoperibolic calorimetry to assess the effect of zinc on cement hydration
*Journal of Thermal Analysis and Calorimetry. Cham: Springer International Publishing*
133(1) pp 27–40