The products of a high temperature reaction of fly ash with lime and soda

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Abstract. A composition of coal combustion fly ash depends on a coal composition and conditions of a combustion process. The main components are SiO₂ and Al₂O₃. An amount of Al₂O₃ in coal combustion fly ash is relatively high, about 30–40%, and for this reason, the fly ash could be potentially used as a raw material source for alumina production. There are several ways to get alumina. The fly ash could be acid leached or sintered with a suitable additive. One of the possible sintering processes is lime-soda sinter process. The article deals with products of lime-soda sinter process of the fly ash produced from brown coal in Czech thermal power plant. The phase composition of sintered material was determined by X-ray diffraction analysis (XRD). The presence of sodium aluminate and dicalcium silicate was confirmed.

1. Introduction

Global production of alumina (Al₂O₃) was 132 million tonnes in 2017 [1]. Over 95% of the alumina is made from bauxite by Bayer process. Bauxite ores contain about 30–60% of aluminium oxide [2]. Bayer process is a complex process which involves five major steps: grinding and pre-treatment of bauxite, pressure digestion in caustic liquor, separation of red mud (insoluble residues) from a caustic solution containing alumina, precipitation of alumina hydrate and its separation from impurities, calcination at high temperature [3].

Fly ash is a by-product of a coal combustion process in thermal power plants. Its composition depends on the type and composition of coal and combustion process conditions. Majority of fly ashes produces in the Czech Republic are made from brown coal. The major components of high-temperature coal combustion fly ashes are SiO₂, Al₂O₃, Fe₂O₃, TiO₂, CaO. An amount of aluminium oxide in Czech fly ashes reaches about 30% [4, 5]. Therefore, fly ash could be used as a raw material for alumina production.

There are several types of processes of alumina production from coal combustion fly ash: leaching processing, whereas leaching agent is usually used acid [6, 7], sintering processing used several types of sintering agents [8, 9] and combinations of leaching and sintering processes or other special processes [10–12].

Sintering processes are high-temperature reactions of the alumina ores with sintering additives. The sinter is leached to extract soluble Al₂O₃ compounds. The Al₂O₃ precipitate from leach liquors in a purified form [13]. Lime-soda sinter process used as sintering additives CaCO₃ (lime) and Na₂CO₃ (soda). The reaction is carried out at temperatures above 1100°C. The main products of the reaction are water-soluble sodium aluminate (NaAlO₂) and water-insoluble (2CaO·SiO₂) [14]. Sintered material is
solved in water or diluted alkali solution [15]. The reaction of sintering additives with fly ash is quite similar to the reaction of kaolinite (1) [16]:

$$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 4\text{CaCO}_3 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + 2(2\text{CaO} \cdot \text{SiO}_2) + 5\text{CO}_2 + 2\text{H}_2\text{O}$$

(1)

In addition to the mentioned main phases, others such as calcium aluminates, CaO-Al$_2$O$_3$-SiO$_2$ and Na$_2$O-Al$_2$O$_3$-SiO$_2$ compounds may arise [16]. The low C/S (CaO/SiO$_2$) molar ratio can lead to insoluble Na$_2$O·Al$_2$O$_3$·2SiO$_2$. On the contrary, the high C/S molar ratio, in turn, promotes the formation of insoluble 4CaO·Al$_2$O$_3$·Fe$_2$O$_3$. Both cases lead to losses of Al$_2$O$_3$ [9].

The paper studied the phase composition of the sintered material and the influence of the ratio of sintering additives to it.

2. Experimental

2.1. Materials

High-temperature brown coal combustion fly ash from Czech power plant, soda (Na$_2$CO$_3$) and lime (CaCO$_3$) were used for samples preparation. Phase composition of fly ash was determined by XRD on the device Empyorean (Panalytical) (see table 1). The chemical composition of used fly ash was examined by X-Ray fluorescence on the device Xenemetric EX-6600 SSD. The content of major oxides is given in table 2, other oxides were present in an amount less than 0.2%.

| Table 1. The phase composition of fly ash. (++ majority phase, ++ significant phase, + minority phase) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Mullite         | Quartz          | Hematite        | Magnetite       | Amorphous       |
| +++             | ++              | +               | +               | +++             |

| Table 2. The chemical composition of fly ash (major oxides) [wt. %]. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| SiO$_2$         | Al$_2$O$_3$     | CaO             | Na$_2$O         | K$_2$O          |
| 47.3            | 29.8            | 4.31            | 0.88            | 1.51            |
| MgO             | SO$_3$          | Fe$_2$O$_3$     | TiO$_2$         | P$_2$O$_5$      |
| 1.29            | 1.06            | 19.2            | 1.43            | 0.27            |

2.2. Samples preparation

Fly ash was mixed with sinter additives, sodium and calcium carbonates. The amount of additive was such that N/A molar ratio was between 1.3–1.8, where N means Na$_2$O from Na$_2$CO$_3$ and A means Al$_2$O$_3$ from the fly ash. The value of C/S molar ratio was between 2.0–2.3, where the C means CaO from CaCO$_3$ and S means SiO$_2$ from the fly ash. In the sample name, the first number means N/A, the second number means C/S. The list of prepared samples is summarized in the table 3. The table 4 shows weight of sinter additives for individual molar ratios.

| Table 3. The list of prepared samples (N/A= Na$_2$O/Al$_2$O$_3$ molar ratio, C/S= CaO/SiO$_2$ molar ratio). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Name            | N/A             | C/S             | Name            | N/A             | C/S             | Name            | N/A             | C/S             |
| P_1.3_2.0       | 1.3             | 2.0             | P_1.3_2.1       | 1.3             | 2.1             | P_1.5_2.2       | 1.5             | 2.2             |
| P_1.4_2.0       | 1.4             | 2.0             | P_1.4_2.1       | 1.4             | 2.1             | P_1.6_2.2       | 1.6             | 2.2             |
| P_1.5_2.0       | 1.5             | 2.0             | P_1.5_2.1       | 1.5             | 2.1             | P_1.7_2.2       | 1.7             | 2.2             |
| P_1.6_2.0       | 1.6             | 2.0             | P_1.6_2.1       | 1.6             | 2.1             | P_1.8_2.2       | 1.8             | 2.2             |
| P_1.7_2.0       | 1.7             | 2.0             | P_1.7_2.1       | 1.7             | 2.1             | P_1.8_2.3       | 1.8             | 2.3             |
| P_1.8_2.0       | 1.8             | 2.0             | P_1.8_2.1       | 1.8             | 2.1             |                  |                  |                  |
Table 4. Weight of sinter additives for individual molar ratios.

|   | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 |
|---|-----|-----|-----|-----|-----|-----|
| m (Na₂CO₃) [g/1 g fly ash] | 1.41 | 1.52 | 1.63 | 1.73 | 1.84 | 1.95 |
| C/S | 2.0 | 2.1 | 2.2 | 2.3 |     |     |
| m (CaCO₃) [g/1 g fly ash]  | 5.52 | 5.79 | 6.07 | 6.35 |     |     |

The mixture was homogenized in a vibratory mill for 60 s. Tablets with diameter 13 mm and high 5 mm were pressed from the homogenized mixture. The compressing pressure was 4 MPa and the compressing time was 3 min. The tablets were sintered on a platinum pod in a laboratory furnace at 1250°C for 30 min (heating rate 5°C/min; cooling rate 3°C/min to 500°C and then natural cooling).

The morphology of sintered tablets was determined by scanning electron microscope (SEM) on the device ZEISS EVO LS 10. The composition of sintered material was analyzed by X-Ray diffraction (XRD).

3. Results and discussion

The mixture of fly ash, lime and soda was pressed to tablets for studying the products of lime-soda sinter process. The figure 1 shows that tablets shrunk and changed the colour after the sintering process. The shrinking of tablets is a result of sodium and calcium carbonate decomposition. Because of the high-temperature of reaction carbonate oxide evaporate and the resulting structure is sintered.

The morphology of sintered tablets was observed by SEM and the example can be seen in figure 2.

![Figure 1. Tablets before (left) and after (right) sintering.](image)

![Figure 2. The microstructure of sample P_1.6_2.0, 10 000 × (left) and 2 000 × (right) (SEM).](image)

The phase composition of sintered material was studied on four series of samples. The difference was in the N/A and C/S molar ratios. The results of XRD analyses are shown in figures 3–6. Figure 3 shows the phase composition of sintered samples with the C/S molar ratio of 2.0. The N/A molar ratio differ from 1.3 (bottom) to 1.8 (up). The major phase in all samples is Ca₂SiO₄ (2CaO·SiO₂), which is a reaction product of silicon phases from fly ash and CaO [17]. It is very slowly soluble in
water, what makes it possible to separate it from alumina phases [18]. The next silicate phase which is present in all samples is Na₂Ca₃Si₂O₈. Its content decreases with increasing N/A molar ratio. In samples with N/A molar ratio from 1.3 to 1.7 is present SiO₂ (quartz). Quartz is an unreacted fly ash component. Its content increases with increasing N/A molar ratio to N/A = 1.6, its amount is minimal in sample P_1.7_2.0. In samples with N/A = 1.3–1.7 is present SiO₂ (quartz). Quartz is an unreacted fly ash component. Its content increases with increasing N/A molar ratio to N/A = 1.6, its amount is minimal in sample P_1.7_2.0. In samples with N/A = 1.3–1.7 are present aluminium-silicate phases as NaAlSiO₄, Na₈Al₄Si₄O₁₈, Na₁.₉₅(Al₁₉₅Si₀₅O₄). The occurrence of such phases is undesirable because it decreases alumina recovery [16]. The phase which is desired because it is well soluble in water and is thus suitable for the separation of alumina is NaAlO₂ [18]. Sodium aluminate is present in sample P_1.7_2.0 and P_1.₈_2.0, whereas in sample P_1.₈_2.0 NaAlO₂ is the only aluminium phase. So for the C/S = 2.0 is the ideal N/A molar ratio of 1.8.

In the series with C/S = 2.1 which is shown in figure 4 the situation is quite similar. The main phase in all samples is Ca₂SiO₄. Quartz is present in samples with N/A = 1.3–1.7, whereas the highest amount of it is in P_1.₅_2.₁. Sodium-calcium silicates (Na₂Ca₃Si₂O₈, Na₂CaSiO₄) are present in all samples. Their amount decreases with increasing N/A molar ratio. Aluminium-silicate phases NaAlSiO₄, Na₈Al₄Si₄O₁₈ were detected just in samples with low N/A molar ratio, N/A = 1.₃ and 1.₄, but Na₁.₉₅(Al₁₉₅Si₀₅O₄) is in all samples except P_1.₈_2.₁. Sodium aluminate, as desired aluminium phase, is present from N/A = 1.₅. Its amount increases with increasing N/A molar ratio. In samples with N/A = 1.₅–1.₇ NaAlO₂ exists next to Na₁.₉₅(Al₁₉₅Si₀₅O₄), in P_1.₈_2.₁ the sodium aluminate is the only aluminium phase. So the ideal N/A ratio for C/S = 2.₁, similar to C/S = 2.₀, is 1.₈.

The results described above show, that N/A = 1.₃ and 1.₄ are too low. The samples contain a large number of phases. Aluminium is located in various aluminium-silicate phases and NaAlO₂ is not present.

In the series with C/S = 2.₂ contain four samples with N/A from 1.₅ to 1.₈. All samples of the series contain Ca₂SiO₄, Na₂CaSiO₄ and NaAlO₂. P_1.₅_2.₂ contains quartz, as unreacted phase, Na₂Ca₃Si₂O₈, Na₂Ca₃Si₃O₁₀ and aluminium-silicate phases NaAlSiO₄ and Na₁.₉₅(Al₁₉₅Si₀₅O₄). Although the sample contains NaAlO₂ which allows the separation of aluminium, the chosen ratio is not suitable since the presence of aluminium-silicates will reduce the efficiency of the process. Combination of N/A = 1.₆ and C/S = 2.₂ is not suitable, too. The sample still contains small amount of aluminium-silicate NaAlSiO₄ and quartz, which amount is higher than in sample P_1.₅_2.₂. The amount of NaAlO₂ is higher and it increases with increasing N/A molar ratio. The phase composition of samples P_1.₇_2.₂ and P_1.₈_2.₂ seems to be very similar. There are present only three phases, Ca₂SiO₄, NaAlO₂ and

\[K = \text{NaAlO}_₂, \quad F = \text{Na}_₂\text{CaSiO}_₄, \quad L = \text{Ca}_₂\text{SiO}_₄, \quad S = \text{Na}_₂\text{Ca}_₃\text{Si}_₂\text{O}_₈, \quad Q = \text{SiO}_₂, \quad N = \text{NaAlSiO}_₄, \quad A = \text{Na}_₁.₉₅(\text{Al}_₁₉₅\text{Si}_₀₅\text{O}_₄), \quad R = \text{Na}_₈\text{Al}_₄\text{Si}_₄\text{O}_{₁₈}\]

Figure 3. The phase composition of sintered samples with N/A = 1.₃–1.₈ and C/S = 2.₀ (XRD).

Figure 4. The phase composition of sintered samples with N/A = 1.₃–1.₈ and C/S = 2.₁ (XRD).
Na$_2$CaSiO$_4$. NaAlO$_2$ is the only aluminium phase, thus means both samples are suitable for alumina recovery. The last series, with the C/S = 2.3, contains four samples. Two samples with higher N/A molar ratio (N/A = 1.7 and 1.8) contain just desired phases, Ca$_2$SiO$_4$, NaAlSiO$_4$ and Na$_2$CaSiO$_4$. In the samples with lower N/A molar ratio (N/A = 1.5 and 1.6), there are present NaAlSiO$_4$ and quartz. Their amount decreases with increasing N/A molar ratio.

Figure 5. The phase composition of sintered samples with N/A = 1.5–1.8 and C/S = 2.2 (XRD).

Figure 6. The phase composition of sintered samples with N/A = 1.5–1.8 and C/S = 2.3 (XRD).

K = NaAlO$_2$, F = Na$_2$CaSiO$_4$, L = Ca$_2$SiO$_4$, S = Na$_2$Ca$_3$Si$_2$O$_8$, Q = SiO$_2$, N = NaAlSiO$_4$, A = Na$_{1.95}$(Al$_{1.95}$Si$_{0.05}$O$_4$)

The results of our experiments show, that for sintering temperature 1250°C and sintering time 30 min is for the lime-soda sinter process the most suitable sample P$_{1.7_2.2}$ or P$_{1.8_2.0}$. Samples with higher ratio have the same phase composition, but they are not economically advantageous. An overview of the phases present in each sample is given in the table 5.

Our results do not coincide with the conclusions of the work [16]. Padilla and Sohn achieved the best aluminium recovery at comparable temperature and time (1200–1250°C and 20–30 min), but the ratios of sintering additives to fly ash were significantly lower. According to the results of their experiments, the best conditions were described as N/A molar ratio of 1.3 and C/S molar ratio of 1.7–1.8. Bai et. al. in their article [9] write, that the best conditions of the process are 1200°C, 60 min, C/S = 2.0 and N/A = 0.98. Even if the sintering time is twice time longer, N/A molar ratio is half in according to our experiments. It is likely that the lime-soda sinter process will be heavily influenced by the specific composition of fly ash, so it will not be possible to generalize the ideal conditions.
**Table 5.** The list of phases present in sintered samples.

| Phase                      | P_1.3_2.0 | P_1.4_2.0 | P_1.5_2.0 | P_1.6_2.0 | P_1.7_2.0 | P_1.8_2.0 | P_1.3_2.1 | P_1.4_2.1 | P_1.5_2.1 | P_1.6_2.1 | P_1.7_2.1 | P_1.8_2.1 |
|---------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| NaAlO$_2$                 |           |           |           |           |           |           |           |           |           |           |           |           |
| Na$_{1.95}$Al$_{1.95}$SiO$_4$ |           |           |           |           |           |           |           |           |           |           |           |           |
| NaAlSiO$_4$               |           |           |           |           |           |           |           |           |           |           |           |           |
| Na$_8$Al$_4$Si$_4$O$_{18}$ |           |           |           |           |           |           |           |           |           |           |           |           |
| SiO$_2$                   |           |           |           |           |           |           |           |           |           |           |           |           |
| Ca$_2$SiO$_4$             |           |           |           |           |           |           |           |           |           |           |           |           |
| Na$_2$Ca$_2$Si$_2$O$_8$   |           |           |           |           |           |           |           |           |           |           |           |           |
| Na$_2$CaSiO$_4$           |           |           |           |           |           |           |           |           |           |           |           |           |

4. **Conclusion**

The presented work focused on the lime-soda sinter process as a possible method for aluminium recovery from the brown coal combustion fly ash. Lime and soda were used as sintering additives. The essence of the process is to convert the aluminium components of the fly ash to water-soluble sodium aluminate and the silicate phases of the fly ash to insoluble dicalcium silicate. Sintering temperature 1250°C and sintering time 30 min were used in experiments. Sodium aluminate as the only aluminium phase in the sintered material was in samples with N/A = 1.8 and C/S = 2.0, 2.1, 2.2, 2.3 and in samples with N/A = 1.7 and C/S = 2.2, 2.3. The next phases present in the said samples were dicalcium silicate and sodium-calcium silicates. With regard to the economic aspect, the best samples for alumina recovery are sample with N/A = 1.7 and C/S = 2.2 and sample with N/A = 1.8 and C/S = 2.0.

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