Possibilities of fly ash activation in alumina recovery process

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Abstract. This paper summarises various possibilities of high-temperature fly ash (HTA) and fluidised-bed filter ash (FFA) activation in metal and oxides recovery processes (esp. alumina recovery). The study deals with chemical and phase composition ash modification to improve leachability of aluminium compounds into sulphuric acid solution. Samples of HTA and FFA produced by power plant industry in the Czech Republic were subjected to diverse types of modification, such as sulphuric acid concentration, ash/acid ratio and sintering reactions using several types of solid agents. Sintering reaction were based on forming acid soluble calcium aluminates via donating the system with calcium oxide, - carbonate and - chloride. Phase and chemical composition were characterised by means of XRD and XRF analysis and the concentration of Al in acid solutions via ICP–OES. Appropriate modification of input material by high-temperature sintering reaction using calcium chloride combined with extraction into 10 wt. % sulphuric acid leads to dissolution up to 99% of aluminium from FFA and up to 94% form HTA. At least, irreplaceable dopant for cement production – gypsum, is formed as a by-product of leaching.

1. Introduction
The use of any energy source comprises some technological advantages and disadvantages, as well as environmental benefits and problems [1]. Worldwide, probably the most typical energy source is still coal. The coal firing power plants produce large amounts of an unburnable rest – fly ash (FA).

FA is generated from the various organic and inorganic components of burned coal at 700–900°C in case of fluidised bed burning and 1 000–1 300°C on a way of classical high–temperature combustion [2, 3]. The worldwide production of FA reaches about 500 mil. tonnes a year [4]. With This large amount of the secondary energy products needs to be stored. This process means deposition of FA mainly in waste ponds. These sludge lagoons could cause environmental contamination and other ecological problems in case of dissolution toxic substances like heavy metals. FA particles are very small (3–80 µm) and could be easily suspended in the air and have become also a major source of gas pollution [5].

Since 1950s many researches on FA application started. Since then the FA is utilised in cement and concrete production because of its pozzolanic properties, because FA react with lime and produce insoluble stable compounds. This category contains about 50% of the utilized FA. [6] Other applications include structural stabilization, waste stabilization, mining applications, agriculture, subbases and other. The Current FA utilization reaches up to 40% in the USA and 47% in Europe [2, 7].

FA could be also strategical source in the search of new material base for the future because many strategical compounds like alumina, titanium oxide, silica as well as some scarce and valuable elements like Li, Rb, Sr, Nb, Ta, Ge, Se, Mo, Ce, Sm, Eu and many other could be recovered from this coal combustion product.
2. Alumina recovery

The alumina recovery from FA was firstly extend in 1950s in Poland due to bauxite embargo during the Cold war [1]. Since then many procedures leading to alumina recovery have been accomplished from the direct acid leaching methods to modified sintering reactions connected with acid or alkali dissolution.

2.1. Direct acid leaching

Direct acid leaching methods (DAL) are based on dissolution of selected components caused by mineral acids, such as sulphuric, nitric, hydrochloric, hydrofluoric or a mixture. DAL could be affected by increasing reaction temperature, FA/acid ratio, acid concentration. Many researches were published on that topic. [8–10] Based on progress results, especially sulphuric acid leaching appears to be one of the most suitable agents for this process. The publications submit a proper FA/acid ratio at least 5:1, sulphuric acid concentration in a range of 30–65 wt. % (approx. 4–10 mol·l$^{-1}$) and they also recommend heating the ash and agent mixture up to 300°C combined with permanent stirring. Higher acid concentration decreases leachability of Al because the incipient aluminium sulphate is not soluble in this medium and sticks on the surface of FA particles. [8]

2.1.1. Sintering reactions. The sintering processes are usually based on a high-temperature reaction between FA and sintering agent to form easily soluble and stable aluminium (or other) compounds [11]. Calcium or sodium reagents could be used as sintering agents. Sintering of aluminium rich FA comes out from the original Pedersen process used in crude iron and calcium aluminate slags production from a mixture of bauxite, iron ore, coke and limestone. [5, 11]

Calcium sinter processes

This process starts with a magnetic separation to remove all magnetic compounds of iron to improve the efficiency. Then FA is mixed with CaO and CaCO$_3$ in a certain FA/agent ratio (1:1 to 1:3) and then is continues with mixture sintering at 1 300–1 400°C. At this temperature, the mullite and quartz phases react together with the calcium agent to form mainly 12CaO·7Al$_2$O$_3$ (mayenite) and 2CaO·SiO$_2$ as a by-product, according to the equations (1–5). Other elements, such as Ti and non-magnetic Fe form CaO·Fe$_2$O$_3$ and CaO·TiO$_2$ respectively, described in equations (6) and (7). [13]

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2, \quad (1)
\]
\[
7(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) + 64\text{CaO} \rightarrow 3(12\text{CaO} \cdot 7\text{Al}_2\text{O}_3) + 14(2\text{CaO} \cdot \text{SiO}_2), \quad (2)
\]
\[
3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 13\text{CaO} \rightarrow 3(3\text{CaO} \cdot \text{Al}_2\text{O}_3) + 2(2\text{CaO} \cdot \text{SiO}_2), \quad (3)
\]
\[
3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 5\text{CaO} \rightarrow 3(\text{CaO} \cdot \text{Al}_2\text{O}_3) + 2(2\text{CaO} \cdot \text{SiO}_2), \quad (4)
\]
\[
2\text{CaO} + \text{SiO}_2 \rightarrow 2\text{CaO} \cdot \text{SiO}_2, \quad (5)
\]
\[
\text{CaO + Fe}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Fe}_2\text{O}_3, \quad (6)
\]
\[
\text{CaO + TiO}_2 \rightarrow \text{CaO} \cdot \text{TiO}_2. \quad (7)
\]

The auto-disintegration process takes place during the cooling below 500°C and it is attributed to the phase modification of generated 2CaO·SiO$_2$. The cooled sinter can be leached by recyclable Na$_2$CO$_3$ solution or by sulphuric acid. According to the research papers, the efficiency of alumina recovery reaches up to 80% depending on a way of dissolution into soda solution or a sulphuric acid. [5, 11, 13]

Another way of mayenite formation in alumina recovery process, using calcium chloride appears to be a suitable reaction agent. This technique simplifies the sintering process by decreasing reaction temperature to about 1 000°C combined with a natural cool down under 600°C. The proper FA/CaCl$_2$ ratio is between 1:0.8 to 1:1.2, depending on FA type. These high-temperature reactions could be described in equations (8–10).
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\[ 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 6\text{CaCl}_2 + \text{SiO}_2 + 6\text{H}_2\text{O} \rightarrow 3(2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Si}_2\text{O}_5) + 12\text{HCl}, \]  
\[ 3\text{SiO}_2 + 3\text{CaCl}_2 + \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 + 6\text{HCl}, \]  
\[ 7(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) + 36\text{CaCl}_2 + 36\text{H}_2\text{O} \rightarrow 3(12\text{CaO} \cdot 7\text{Al}_2\text{O}_3) + 14\text{SiO}_2 + 72\text{HCl}. \] 

This method is also followed by sulphuric acid leaching to recover up to 97% of alumina. The course of acid leaching could be described in equations (11) and (12). [15]

\[ 3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 + 6\text{H}_2\text{SO}_4 \rightarrow 3\text{CaSO}_4 \downarrow +3\text{H}_2\text{SiO}_4 \downarrow +\text{Fe}_2(\text{SO}_4)_3, \]  
\[ 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 + 33\text{H}_2\text{SO}_4 \rightarrow 12\text{CaSO}_4 \downarrow +7\text{Al}_2(\text{SO}_4)_3 + 33\text{H}_2\text{O}. \]

3. Materials and methods

3.1. Raw materials

One sample of HTA (type 1) and FFA (type 2) from the Czech Republic production were used to undergo a couple of sintering reactions described above (CaO, CaCO$_3$ and CaCl$_2$ agents). At first, samples of FA were dried in laboratory dryer at 105°C to constant weight. Then a fraction with particle size lower than 63 µm was sieved. Then the chemical and phase composition, specific area and loss on ignition were determined. The used CaO and CaCO$_3$ agents were commercial sources; the lime with a specification Cl 90Q (min. free lime content of 90%) and the calcite very finely grounded (max. impurity content of 5%). The CaCl$_2$ agent was used in a p. a. form.

3.2. Sintering reactions conditions and leaching

Calcium oxide and calcium carbonate sintering reactions were carried out in super-kanthal laboratory furnace using temperature protocol as follows – lab. temperature to 1 250°C with a heating rate of 10°C·min$^{-1}$, followed by constant temperature at 1 250°C for 60 min, the cooling rate of 5°C·min$^{-1}$ to 600°C and then a natural cooling to laboratory temperature. Sintering with calcium chloride agent was done in laboratory muffle furnace heating to 1 000°C, other parameters of the temperature protocol were the same as described above. The amounts of sintering agents were chosen as follows: agent/FA 0.5, 1.0 and 1.5; in case of CaCl$_2$ mixtures containing 0.6, 0.8 chloride agent have been prepared extra. All these mixtures were homogenised in a sealed bottle on a rotary shaker.

Clinker was disintegrated in a mortar and characterised by x-ray fluorescence spectrometry XRF (Olympus Delta professional) and x-ray diffraction XRD (Panalytical Empyrean) after sintering reaction. The samples of modified FA were subjected to dissolution of Al content into the sulphuric acid solution with acid/FA ratio of 15. Concentration of Al in the acid solution was quantified by inductively coupled plasma optical emission spectroscopy ICP–OES (Horiba Scientific – Ultima 2). The extraction of Al into sulphuric acid was performed using laboratory magnetic stirrer with constant stirring speed of 250 rpm.

4. Results

4.1. Raw materials

Results of the chemical composition determined by XRF method are given in table 1. The XRD Rietveld analysis showed presence of quartz, cristobalite, magnetite and mullite phases in case of the high-temperature FA and quartz, anhydrite, lime, calcite, portlandite, hematite, anatase and muscovite phases in FFA. The density ($D$) of FA was determined using pycnometer method using isopropyl alcohol as the immersion liquid. The specific surface area was measured by Blaine. The free lime content in FA samples was qualified by saccharose titration method. All these results inclusive loss on drying (LOD) and loss on ignition (LOI) are summarized in table 2.
Table 1. Chemical properties of FA, part 1.

| Sample       | Al₂O₃ (wt. %) | Fe₂O₃ (wt. %) | TiO₂ (wt. %) | MgO (wt. %) | CaO (wt. %) | SiO₂ (wt. %) | K₂O (wt. %) | Na₂O (wt. %) | SO₃ (wt. %) |
|--------------|---------------|---------------|--------------|-------------|-------------|--------------|-------------|--------------|------------|
| HTA (type 1) | 29.50         | 7.45          | 1.83         | 0.32        | 2.94        | 54.04        | 2.69        | 0.24         | 0.76       |
| FFA (type 2) | 27.93         | 7.03          | 3.36         | 0.38        | 21.24       | 32.07        | 0.93        | 0.47         | 6.42       |

Table 2. Chemical properties of FA, part 2.

| Sample       | D (kg·m⁻³) | Blaine (m²·kg⁻¹) | Free CaO (%) | LOD (%) | LOI (%) |
|--------------|------------|-----------------|-------------|---------|---------|
| HTA (type 1) | 2249       | 315.4           | 7.87        | 23.6    | 0.96    |
| FFA (type 2) | 2716       | 633.6           | 25.65       | 51.3    | 8.81    |

It is obvious that the FA could be quite rich mainly in aluminium, iron and even silicon as well. In some kinds of HTA the content of aluminium oxides reaches up to 35%. To compare with the purity of nowadays bauxite ore of about 45% [15], the content of alumina in FA is not that low. The SiO₂ content prevents the traditional way of aluminium production from the Bayer method.

4.2. Sintered materials

4.2.1. CaO/CaCO₃ sintering. Sintered mixtures of HTA and CaO/CaCO₃ were disintegrated in mortar to give a particle size less than 63 μm. All samples were subjected to determination of unreacted agent as the free lime content using saccharate titration method. These results given in table 3 show that the addition of the sintering agent above 1.5 FA weight could be considered as non-effective.

Table 3. Unreacted amount of reaction agent determination.

| Agent addition (agent/FA) | CaO Free CaO (%) | Unreacted amount (%) | CaCO₃ Free CaO (%) | Unreacted amount (%) |
|---------------------------|-----------------|----------------------|-------------------|---------------------|
| 0.5                       | 7.87            | 23.6                 | 0.96              | 4.8                 |
| 1.0                       | 25.65           | 51.3                 | 8.81              | 26.4                |
| 1.5                       | 40.74           | 77.9                 | 23.39             | 54.6                |

Calcium carbonate addition also affects the porosity of the sintered material, due to the limestone decomposition and release of CO₂, resulting in a pore aggregate in the material, which leads to easier disintegration than the lime addition. To remove the unreacted amount of the sintering agent, the 1 wt. % HCl washing was used. The volume of the washing agent was increased by 30% of the equimolar amount of the free lime. The XRD analysis shows the presence mainly of 12CaO7Al₂O₃ and other calcium-aluminate phases.

To compare leachability of aluminium from sintered and raw (ref) FA, a single-stage extraction into 10 wt. % sulphuric acid at room temperature was tested in laboratory. Leachability of Al was monitored in time using ICP-OES. The results shown in figures 1–4 represent dissolved aluminium contentment (%) in time.
5

Figure 1. Leachability of aluminium with CaO addition into 10 wt. % H₂SO₄ medium; HTA.

Figure 2. Leachability of aluminium with CaCO₃ addition into 10 wt. % H₂SO₄ medium; HTA.

According to the results, there has been a multiple increase of efficiency in Al dissolution than in case of raw FA under the same conditions. From the point of view of leachability, the most optimal is the addition of 1.5 CaO. Up to 44.7% of present Al could be dissolved. In terms of trends it is possible to talk about a similar course of reaction with limestone agent as in the case of CaO addition. From an economic point of view, however, the maximum addition method does not provide very satisfactory results since it obtains a relatively high percentage of unreacted proportion of the sintering. The possibility of the unreacted portion agent removing by washing using a weak solution of hydrochloric acid is easily feasible but prevents the regeneration of the unreacted sintering agent.

4.2.2. CaCl₂ sintering. Sintered mixtures of FA and chloride agent were cooled down at the room temperature. Subsequently, a part of each sample was washed using distilled water and the amount of unreacted chloride was determined by complexometric titration with chelate III. The results are given in table 4.
Table 4. Unreacted amount of reaction agent determination.

| CaCl₂ addition (agent/FA) | HTA Unreacted amount (%) | FFA Unreacted amount (%) |
|---------------------------|--------------------------|--------------------------|
| 0.5                       | 12.5                     | 17.8                     |
| 1.0                       | 24.3                     | 35.3                     |
| 1.5                       | 51.9                     | 58.6                     |

From the results of the unreacted agent amount, the additions above 1.0 already might appear to be ineffective as it does not react with the FA. Selected samples of water washed, and non-washed materials were further extracted into 10 wt. % sulphuric acid to compare the leachability of Al in the previous method. Based on the results, it was found that the washed samples reached the leachability of Al by 30% higher (table 5).

Table 5. Comparation of Al leachability from water washed and non-washed samples.

| CaCl₂ addition (agent/FA) | non-washed | washed |
|----------------------------|------------|--------|
| 0.6                        | 27.92      | 61.77  |
| 0.8                        | 36.14      | 83.51  |
| 1.0                        | 65.38      | 93.32  |

Figure 3. Leachability of aluminium with CaCl₂ addition into 10 wt. % H₂SO₄ medium; HTA, washed.
By comparing the results of leaching of HTA and FFA, this method could be referred to as universal and fully applicable for both types of FA. In terms of HTA, the optimum addition of CaCl$_2$ reaches 1.0, in case of FFA the sufficient addition is 0.8. As can be seen in the charts, it is possible to separate up to 99% of aluminium. The given method is even relatively selective for leaching Al, since dissolution max. 4% Ti and max. 27% Fe. The chloride addition could also reach the leachability of Al two times higher compared to the addition of CaO. The course of the experiment was carried out in accordance to article [15] with the achievement of similar results. According to these data, the calcium chloride method could be probably used in other types of fly ash and other materials.

5. Conclusion

Within the scope of increasing the leachability of aluminium from HTA and FFA, some methods of chemical reaction were laboratory tested. FA phase composition modification by sintering with various melt-inducing agents forming of new, especially, calcium-aluminate phases have been evaluated. Modification of the FA composition using CaO in a high temperature reaction at 1 250°C gives a possibility to grow the efficiency of Al dissolution into 10 wt. % sulphuric acid up to 45%. In case of FA modified by addition of CaCl$_2$ and sintered at 1 000°C, it is possible to dissolve up to 99.3% Al. Based on the obtained results, sintering reaction with CaCl$_2$ could be labelled as a universal method for both types of FA (HTA and FFA). At the same time, this method seems to be also very selective and offers the possibility of unreacted sintering agent regeneration.

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