Fly Ash as a Material for Thermochemical Energy and CO_2 Storage

Saman Setoodeh Jahromy, Christian Jordan, Michael Harasek and Franz Winter

Incineration of municipal solid waste is a reasonable technique that is used to manage the huge amounts of waste generated in urban areas. However, this technique produces fly ash, which is disposed of often after a stabilization process.

Fly ash may be rich in heavy metals. Therefore, technologies for metal recovery on a large scale are developed such as the FLUREC technology [12]. Additionally, owing to the similar chemical composition of fly ash with the cement, its usage as an additive in the field of construction (cement, concrete, and ceramics) as well as in geotechnical (roads, pavements), agricultural (soil amendments), and other (sorbents and sludge conditioning) materials on the laboratory scale is still underway [4].

Calcium oxide (CaO) is one of the main components in fly ash, which is a potential candidate material in the field of thermochemical energy storage (TCES) [6]. Therefore, this feasibility study *Waste2Storage* investigates the potential of fly ash generated not only from MSW incinerators but also from other incineration plants of biomass, paper, pulp, and sewage sludge, as a CO_2 storage and TCES material.

1. Thermal energy storage

CO_2 capture and storage, as well as prevention, are among the most critical environmental goals of industry. Following the Kyoto Protocol, in December 2015, 195 countries agreed on a universal, legal, and global protocol to keep global warming below 2 °C to prevent or limit the climate changes. To achieve this goal, the industrial sector must optimize and adopt improved processes [11].

Among the methods that can make this possible is to shift to renewable and sustainable energy sources, to store and utilize CO_2, or to store waste energy that is lost through conversion processes from one type of energy to another, resulting in the conservation of primary sources.

Renewable energy sources, such as concentrated solar power and wind power plants, fluctuate in time. To overcome this drawback and make these energy sources competitive with fossil energy sources, storing excess energy from renewable energy plants is essential. Natural gas plays an important role as a fossil energy source in generating electricity; thus, a considerable part of energy is lost as waste heat through the conversion process. To use this energy and other waste heat streams, thermal energy storage is a promising method, which stores the energy for further use. Thermal energy storage is divided into three categories: sensible heat storage, latent heat storage, and TCES. Sensible heat storage uses materials with a high specific heat capacity, such as water, to store heat. Latent heat storage uses the enthalpy of the phase change of materials (solid/liquid, liquid/gas), such as paraffins and sodium or potassium salts, to store and release heat. Sensible and latent heat storage are considered state-of-the-art methods.

In contrast, TCES is still in the development stage; however, it is a high potential technology owing to its advantages, such as its high energy density, seasonal storage capability, and easy transportation [1, 5]. Currently, the industrial implementation of this technique is the focus of researchers worldwide. For TCES, suitable and affordable materials are required. There are well-known materials that are good candidates for TCES at different temperature levels, such as metal oxides and salt hydrates [2, 3, 10, 13]. Nevertheless, raw materials have some drawbacks such as sintering effects, slow conversion rate (reaction kinetics), and low cycle stability. Therefore, researchers have attempted to overcome these problems by doping or mixing them with suitable materials [9]. However, the materials that can fulfil these requirements for utilization as a TCES material from technical, ecological, and environmental standpoints are still under development; and to our knowledge, no by-products or waste from industry for utilization as TCES have been investigated thus far [7].

2. Thermochemical energy storage

TCES is a new technology compared to the sensible and latent heat storage technologies. It is based on reversible exothermic and endothermic chemical reactions. Excess thermal heat, for example from renewable energy sources, is used to decompose component $A_{(s)}$ via an endothermic reaction into its components $B_{(s)}$ and $C_{(g)}$ (charging step). Component $B_{(s)}$ is stored for a period of time until thermal heat is required, and the energy is released by the exothermic reaction with component $C_{(g)}$ (discharging step) [3]. Equation (1) illustrates a reversible gas-solid reaction that is preferable owing to its easy separation between gas and solid phases of the products.

$$A_{(s)} + \Delta H \leftrightarrows B_{(s)} + C_{(g)} \qquad (1)$$

Figure 1 shows the principle of TCES.

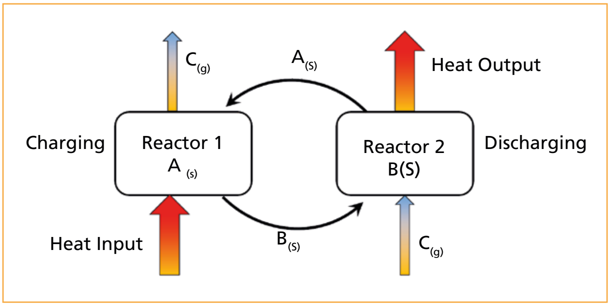

Figure 1:
Principle of thermochemical energy storage

Source: Deutsch, M.; Müller, D.; Aumeyr, C.; Jordan, C.; Gierl-Mayer, C.; Weinberger, P.; Winter, F.; Werner, A.: Systematic search algorithm for potential thermochemical energy storage systems. In: Applied Energy, 183 ,2016, 113-120. Retrieved July 2019 from: https://doi.org/10.1016/j.apenergy.2016.08.142.

3. Fly ash as a thermochemical energy storage material

As mentioned above, the potential of wastes or by-products from industry to be utilized for TCES has not been studied so far. Fly ash contains a considerable amount of calcium oxide (CaO). A special feature of CaO is its ability to react with water vapour or CO_2 [7]. Thus, two TCES systems with relatively high-energy densities can be built on the basis of CaO, presented as follows:

$$CaO_{(s)} + H_2O_{(g)} \leftrightarrows Ca(OH)_{2(s)} + \Delta H \qquad (2)$$

$$CaO_{(s)} + CO_{2(g)} \leftrightarrows CaCO_{3(s)} + \Delta H \qquad (3)$$

Calcium carbonate ($CaCO_3$) and calcium hydroxide [$Ca(OH)_2$] have a theoretical energy content of 1.66 MJ/kg and 1.35 MJ/kg, respectively. For Reaction 3, CO_2 can be stored by harvesting energy simultaneously. Another benefit of the fly ash carbonation is the stabilization of harmful metal components existing in fly ash [14].

Therefore, it is interesting to investigate fly ash for its utilization as a TCES and CO_2 storage material. To use fly ash as a TCES material, it should meet at least the following requirements [8]:

- Reversible endothermic reaction of the fly ash (discharged form) during thermal treatment:
  $A_{(s)} + \Delta H \leftrightarrows B_{(s)} + C_{(g)}$
- Reversible exothermic reaction of the charged form, $B_{(s)}$, with gaseous components:
  $B_{(s)} + C_{(g)} \leftrightarrows A_{(s)} + \Delta H$
- Cycling stability (charging and discharging of heat)

After meeting the above three requirements, other criteria such as price, toxicity, availability, and corrosion will matter.

4. Experimental results

The X-ray fluorescence results for the analysed fly ash samples from different industrial segments confirmed that CaO is one of the main components in all samples and its content varies between 10 and 65 %. The first requirement, endothermic reactions through thermal treatment, was successfully accomplished for several fly ash samples during simultaneous thermal analysis (STA), except for a few of them. The second requirement, exothermic reactions of the charged form with gaseous components, such as CO_2, H_2O, and CO_2/H_2O, could be met only for a few of the fly ash samples.

Figure 2 shows one STA experimental run for the charging step up to 880 °C at a heating rate of 30 K/min under a N_2 atmosphere and subsequent discharging under a pure CO_2 atmosphere at a cooling rate of 10 K/min. During the charging step, the mass signal decreased (thermogravimetric analysis [TGA], green line), which was followed by endothermic peaks identified via differential scanning calorimetry (DSC) (blue line). During the cooling phase, the mass signal increased following the exothermic reaction of CO_2 with the charged form of the fly ash.

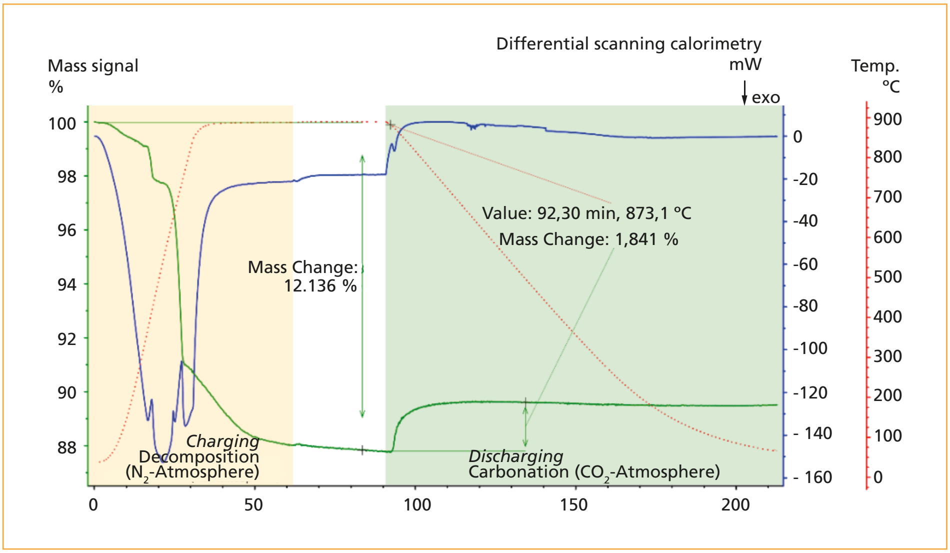

Figure 2: Charging up to 880 °C under a N_2 atmosphere and discharging under a pure CO_2 atmosphere; the mass signal is shown by a green line, the DSC is shown by a blue line, and the temperature profile is shown by a red dotted line

Source: Jahromy, S.S.; Birkelbach, F.; Jordan, C.; Huber, C.; Harasek, M.; Werner, A.; Winter, F.: Impact of Partial Pressure, Conversion, and Temperature on the Oxidation Reaction Kinetics of Cu_2O to CuO in Thermochemical Energy Storage. In: Energies, 12, 2019, 508. Retrieved July 2019 from: https://doi.org/10.3390/en12030508.

In another STA experiment for comparison with the previous one, a mixture of CO_2 (100 ml/min) and H_2O (1 g/h) was used for the reverse exothermic reaction (discharging/energy harvesting). Figure 3 shows the positive impact of water vapour on the carbonation reaction for this kind of fly ash.

The energy content of the examined fly ash samples was between 100 and 500 kJ/kg based on charging and discharging. This energy content of the waste/by-product material is not negligible compared to the theoretical energy contents of other metal oxides Co_3O_4/CoO ~ 844 kJ/kg, CuO/Cu_2O ~ 810 kJ/kg, MnO_2/Mn_2O_3 ~ 480 kJ/kg, and Mn_2O_3/Mn_3O_4 ~ 202 kJ/kg in TCES [8, 9].

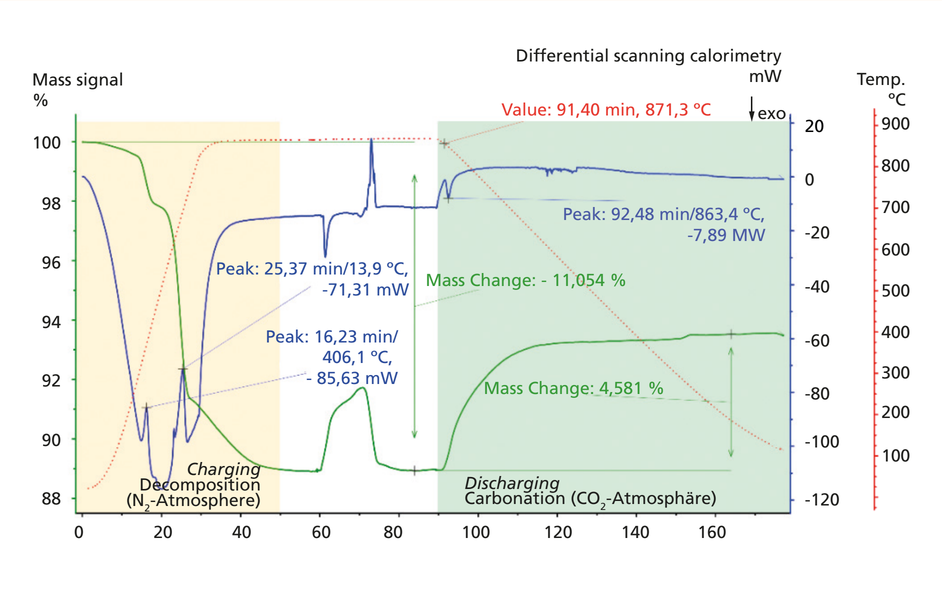

Figure 3: Charging up to 880 °C under a N_2 atmosphere and discharging under a CO_2/H_2O atmosphere; the mass signal (TG) is shown by a green line, the DSC is shown by a blue line, and the temperature profile is shown by a red dotted line

Source: Jahromy, S.S.; Birkelbach, F.; Jordan, C.; Huber, C.; Harasek, M.; Werner, A.; Winter, F.: Impact of Partial Pressure, Conversion, and Temperature on the Oxidation Reaction Kinetics of Cu_2O to CuO in Thermochemical Energy Storage. In: Energies, 12, 2019, 508. Retrieved July 2019 from: https://doi.org/10.3390/en12030508.

The third requirement for a TCES material, cycling stability, was determined via STA for three cycles for a selected fly ash sample. At a heating rate of 30 K/min under the nitrogen atmosphere (charging step), 30 mg of sample was heated up to 880 °C; after a stabilization time of 30 minutes, the atmosphere was changed to a mixture of CO_2 and water vapour (1 g/h) at a cooling rate of 10 K/min from 880 to 350 °C and was maintained at 350 °C for 30 minutes. This cycle was executed three times [7]. Figure 4 presents the result of the three cycle stability run for a fly ash sample. Same mass decrease and increase of about 4 % for charging and discharging step could be identified, respectively, except for the first mass decrease, which was 15.5 %, owing to the decomposition of organic compounds, sulphate, and vaporization of heavy metals with low boiling point, such as Zn and Cd, or the chloride components of metals [8, 7].

Nonetheless, some samples showed a slight decrease in reactivity after each set of cycles (beginning from the first cycle).

Regarding carbon dioxide storage of fly ash, some fly ash samples were able to store CO_2 between 2 (w/w) and 6 % (w/w) of their mass as received under a pure CO_2 atmosphere between 400 and 500 °C (carbonation time of 4 hours) based on the results of the STA.

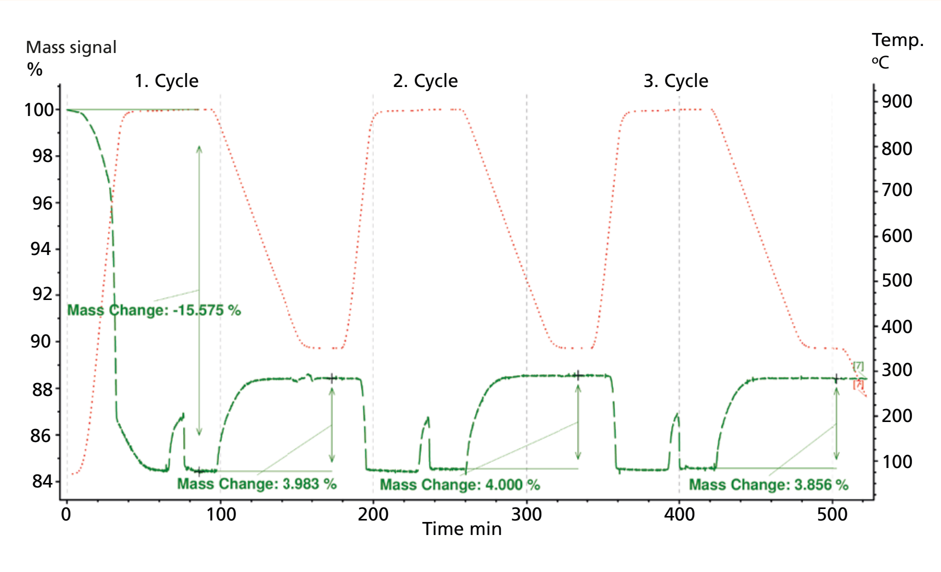

Figure 4: Charging up to 880 °C under N_2 atmosphere and discharging under a CO_2/H_2O atmosphere; the mass signal (TG) and the temperature profile are indicated by a green line and a red dotted line, respectively

Source: Jahromy, S. S.; Azam, M.; Huber, F.; Jordan, C.; Huber, C.; Schwendtner, K.; Neuwirth, E. ; Laminger, T.; Werner, A.; Harasek, M.: Comparative characterization study of fly ashes from different types of incinerators for their potential as thermochemical energy and CO_2 storage material. In: Materials 2019, submitted.

5. Conclusions

The aim of this feasibility study, *Waste2Storage*, is to provide an answer to the question of whether new applications for fly ash generated from different industrial sectors are possible for CO_2 and TCES materials.

The results showed that there is potential for new applications for some types of fly ash samples. Carbonation of fly ash leads to controlled stabilization of the samples, followed by harvesting of energy through an exothermic carbonation reaction. Carbonation of fly ash samples provides another advantage, which is the immobilization of some heavy metals, resulting in better products for further use or maybe for decreasing the amount of cement used in the stabilization processes before landfilling.

However, from an economical point of view, a life cycle analysis and reasonable system integration need to be performed as well.

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Contact person

Dipl.-Ing. Saman Setoodeh Jahromy
Vienna Technical University
Project Assistant
Institute of Chemical, Environmental and Bioscience Engineering
Getreidemarkt 9
1060 Vienna
AUSTRIA
+43 158801166368
saman.setoodeh.jahromy@tuwien.ac.at

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